Nueces Bay TMDL Project for Zinc in Oyster Tissue

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Dedication

I dedicate this work to my parents for their support and their unconditional love.

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Abstract

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The University of Texas at Austin, 2003

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Nueces Bay is on the 303(d) list of impaired water bodies for not meeting the oyster water use due to elevated zinc concentrations in oyster tissue. This work is a preliminary study for the Nueces Bay TMDL project. Information and data about zinc concentrations in water, sediments, oyster tissue and contributing point and non-point sources of zinc in Nueces Bay, are compiled and analyzed. Zinc loadings are determined for each contributing point and non-point source, and a simple water quality-loading model is used to simulate equilibrium concentrations of total zinc in Nueces Bay. Two Continuously Stirred Tank Reactor (CSTR) model scenarios are performed, where loads from the Corpus Christi Inner Harbor through the Central Power and Light (CP&L) station are excluded in the first scenario, and included in the second. Results of the CSTR modeling indicate that high total zinc concentrations in Nueces Bay may be due to the water discharged by the CP&L station from the Corpus Christi Inner Harbor.

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Chapter 1: Introduction

1.1 BACKGROUND AND PROJECT MOTIVATION

Nueces Bay, part of the Coastal Bend Bay system, is surrounded by several industrial plants and refineries. A zinc smelting facility, known as the American Smelting and Refining Company (ASARCO), operated in the region from 1942 to 1985 (TDH, 2003). Currently, on the south side of Nueces Bay a subsidiary of ASARCO named Encycle Texas, Inc., operates a large hydrometallurgical processing complex that chemically recovers the metals in waste and by-product materials received from a variety of manufacturing companies.

Several complaints, originating from a residential neighborhood (Dona Park) of the Corpus Christi area, reported health problems attributed to contamination from the former ASARCO site. Residents also raised concerns about the safety of eating seafood from Nueces Bay. In response to this, the Texas Department of Health (TDH) examined samples of fish, crabs, and oysters from Nueces Bay in August 1994.

Oysters from the 1994 samples contained high concentrations of zinc (range: 2294-2482 ppm), which is above the TDH Health-based Assessment Comparison (HAC) value of 700 ppm. This resulted in a decision by TDH to close Nueces Bay for oyster harvesting and marketing. Based on this information, the Texas Commission on Environmental Quality (TCEQ, former Texas Natural

Resources Conservation Commission) classified Nueces Bay as “impaired” and placed it on the Texas 303 (d) list of impaired waterbodies.

In response to these conditions, a total maximum daily load (TMDL) project has been initiated by TCEQ to determine the measures necessary to restore water quality in Nueces Bay. The goal of a TMDL is to determine the amount (or load) of a pollutant that a body of water can receive and still support its designated uses. This allowable load is then allocated among all the potential sources of pollution within the watershed, and measures to reduce pollutant loads are developed as necessary (TCEQ, 2002).

The work presented in this report is being conducted in support of the Texas Commission on Environmental Quality development of a Total Maximum Daily Load for Nueces Bay. The Center for Research in Water Resources (CRWR) at the University of Texas has been hired to develop a total loadings model of zinc for Nueces Bay. This project originates from a contract between the General Land Office, and the CRWR. Funds from the General Land office were made available through a grant from The National Oceanic and Atmospheric Administration (NOAA).

The first step in the Nueces Bay project was to verify the impairment. In 2002, with funding from the General Land Office, the Texas Department of Health (TDH) reassessed the potential for health risks from consumption of contaminated seafood taken from Nueces Bay. The TDH risk assessment report concluded that consumption of oysters from Nueces Bay constitutes a public health hazard due to excessively high zinc levels found in these species (range:

704–1450ppm). Consequently, the Texas Department of Health determined that it would continue to list Nueces Bay as an area closed to the harvesting of oysters. In addition, the TDH risk assessment found that consumption of spotted seatrout from Nueces Bay constitutes an indeterminate public health hazard, whereas blue crabs or finfish do not currently pose a threat to public health.

1.2 SCOPE OF WORK

An initial step in the TMDL process is to compile and analyze information on the concentrations, and contributing point and non-point sources of zinc in Nueces Bay. Data concerning zinc levels observed in water, sediment and fish tissue in the area of concern is compiled from various sources (i.e., Texas Commission on Environmental Quality, Coastal Bend Bay & Estuary Program, Texas Department of Health, etc.). Additional data necessary for GIS processing and modeling are also assembled (DEM, Precipitation, geospatial data, land use/ land cover, etc.).

An inventory of contributing point and non-point sources of zinc to Nueces Bay is made. The amounts of loads from each source are determined by either using existing information from previous studies, or estimating unknown contributions based on other information sources. GIS tools and capabilities are also used to direct the pre-processing steps to obtain watershed drainage area, and estimate land surface loading from watershed runoff. From these calculations, the relative contributions of the various loading sources are estimated.

The next and final step in this report is to develop a loading model, a continuously stirred tank reactor (CSTR) model of total zinc in the water column, using a mass balance approach. The loads from the model are input to the receiving water to calculate the equilibrium concentrations in the Nueces Bay system. Finally, the resulting total zinc concentrations are compared with those observed in the bay.

1.3 STUDY AREA

Nueces Bay, is a secondary bay in the Coastal bend Bay system, located along the Texas Gulf Coast. It represents TCEQ water quality management segment 2482. Most of Nueces Bay is located in the San Antonio-Nueces coastal basin, with a small portion in the Nueces-Rio Grande coastal basin (Figure 1.1). Nueces Bay is north of the city of Corpus Christi at San Patricio County (Figure 1.2). The system comprising Nueces Bay, Corpus Christi Bay, Oso Bay, Redfish Bay, and portions of the Laguna Madre, forms the Nueces estuary.

Nueces Bay is a small, shallow water body, approximately 14.5 km long and 5 km wide (Caudle, 1995), with a surface area of 74.9 sq km and an average depth ranging from 0.6 to 1.2 m (Barrera et al, 1995). It has an average volume of about 48,970,000 m^3 (USGS, 2001) and salinities ranging from 15 to 30 ppt (Barrera et al, 1995). Annual rainfall in the study area is about 76 cm (30 inches), and annual evaporation is around 145 cm/yr (USGS, 2001). The climate in this region is arid most of the time, except when influenced by freshets and tropical storms, which often result in flooding (TCEQ, 2002).

The primary source of freshwater to Nueces Bay is the Nueces River entering it on the west. This river currently supplies the bay with approximately 2.47 m^3/s of freshwater, as measured in streamflow gauging station near Callalen

(1991-2000), and is responsible for maintaining the estuarine nature of the system. The Nueces River discharges through a broad river delta area with marshes in the tidal portion at the upper end of Nueces Bay. The primary return flow to Nueces Bay is cooling water discharged from Central Power and Light (CP&L) station. The Central Power and Light station, also called Nueces Bay Power station is a steam electric generating plant located one and a half miles west of the Corpus Christi Harbor Bridge in the city of Corpus Christi, Texas. The Power plant withdraws water from the Corpus Christi Inner Harbor for once through cooling water which discharges to Nueces Bay on its southeastern shore. This cooling water averaged 17.35 m^3/s during the period June 1998 - May 2000 (TDPES permit 01244). The flow of cooling industrial water is almost seven times higher than Nueces River inflow to Nueces Bay, as measured in USGS gauging station at Callalen.

Nueces Bay is economically and ecologically important to the surrounding region. Economic activities in and around the bay include petrochemical refining and production, agriculture, manufacturing, recreation, maritime commerce, and tourism. Ecologically, a number of estuarine-dependent species utilize Nueces Bay as an essential nursery and foraging habitat. The Texas Commission on Environmental Quality (TCEQ) has established Nueces Bay as an exceptional quality aquatic habitat and has designated its uses for contact recreation and shellfish harvesting. Potential environmental threats to the bay are reductions of freshwater inflow, brine discharges and spills from local oil and gas production operations and pipelines, dredging, and dredge material disposal (Barrera et al, 1995).

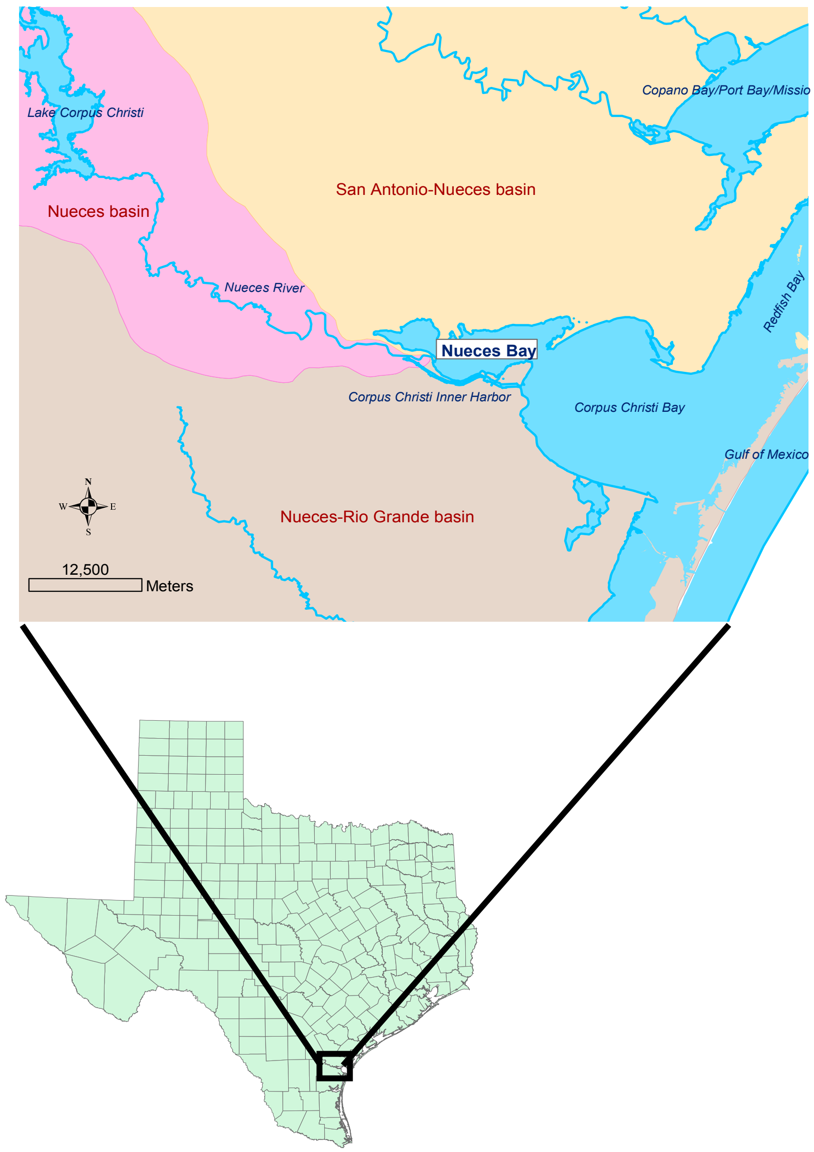


Figure 1.1 Nueces Bay, located along the Texas Gulf Coast

Figure 1.2 Map of Nueces Bay (yellow represents cities)

Chapter 2 – Literature review

2.1 TMDL PROGRAM

A Total Maximum Daily Load (TMDL) is the total amount of a pollutant a water body can receive and still meet state water quality standards. It also refers to the determination of an acceptable constituent load to an impaired stream, lake or estuary, and the allocation of this load between contributing point and nonpoint source pollution in the watershed (TNRCC, 1999).

The goal of TMDL programs is to restore and maintain the water quality in polluted water bodies in Texas, which do not support their beneficial uses. As specified by TCEQ (TNRCC, 1999), the TMDL program involves four processing steps:

- *Identify the water quality target*: this is established by the TCEQ through the Texas Surface Water Quality Standards. The lead organization or stakeholders may also develop additional water quality targets.
- *Assess current watershed and water quality conditions*: gather and collect sufficient water quality data and watershed information to support the analytical need of a TMDL, and determine whether a site-specific modification of water quality standard for the pollutant of concern is appropriate.
- *Analyze pollutant sources (point, nonpoint, natural background, atmospheric deposition)*: identify the geographic location and types of sources of pollution and determine the current and projected pollutant load for each source. Point sources are discharges from a defined outlet.

Examples are discharges from industrial plants, and wastewater treatment plants. Non-point sources are pollution discharges from diffuse, wide geographic areas. Examples include runoff from agricultural and urban areas or deposition of airborne toxics. Natural background sources are those not associated with human activities.

- *Allocate pollutant loads*: among various point, non-point and natural background sources in the watershed using the equation:

  LC = WLA+LA+MOS, where

  Loading capacity (LC) is the maximum amount of pollutant loading a water body can receive without exceeding water quality standards. Waste load allocation (WLA) is the portion of loading capacity allocated to point sources, whereas load allocation (LA) is the portion allocated to nonpoint sources and natural background. MOS is a margin of safety that accounts for uncertainty in determining the amount of pollutant loads.

2.2 FACTS ABOUT ZINC

Zinc is a bluish-white, lustrous metal. It has an atomic number of 30, an atomic mass of 65.38, and belongs to group 2b and the fourth period of the periodic table. Naturally occurring zinc contains five stable isotopes. Twenty-three other unstable isotopes and isomers are also recognized. ^{65}Zn, a radioactive isotope, is the most stable with a half-life of 243.8 days (WHO, 2001).

Zinc is abundant in nature, making up between 0.0005% and 0.02% of the Earth's crust (Irwin et al, 1997). Most zinc ore found naturally in the environment is in the form of zinc sulfide. Zinc compounds are widely used in industry. Their major uses are for galvanizing steel, forming alloys, and producing rubber and paints.

Zinc is an essential food element needed by the body in small amounts. When uptake is too low, deficiency occurs and adverse effects can be observed. On the other hand, too much zinc can lead to toxicity. Between these two extremes, an optimal concentration range for zinc exists for each living organism, including man (Van Assche et al, 1995).

Zinc enters the air, water, and soil as a result of both natural processes and human activities. Most zinc enters the environment as the result of human activities, such as mining, steel production, zinc and other metal manufacturing (WHO, 2001).

2.2.1 Chemical and physical properties

Zinc has a density of 7.13 g/cm^3, which is why it is called a heavy metal. Zinc is a fair conductor of electricity. The metal is too brittle to roll at ordinary temperatures, but it becomes malleable and ductile when heated to 100–150 ºC (WHO, 2001). Zinc has a strong tendency to react with acidic, alkaline and inorganic compounds. At elevated temperatures, zinc reacts strongly with other elements, such as oxygen, chlorine and sulfur (WHO, 2001).

Zinc is commonly present in the divalent state Zn(II). Zn(II) is amphoteric and dissolves in acids to form hydrated Zn(II) cations, and in strong bases to form zincate anions, usually $Zn(OH)_4^{-2}$ (EPA, 1987). Zinc is capable of reducing most metals except aluminum and magnesium (WHO, 2001)

2.2.2 Hazards and toxicity to aquatic life

In the aquatic environment, zinc toxicity is most often associated with elevated concentrations of zinc in water rather than dietary or food chain toxicity (Irwin et al, 1997). Zinc is known to be toxic to many types of aquatic plants and animals, causing mortality, growth retardation, and reproductive impairments (EPA, 1997).

In mammals, excess zinc can cause copper deficiencies, affect iron metabolism, and interact with the chemical dynamics of lead (Irwin et al, 1997). Most aquatic organisms regulate their internal zinc concentrations, and develop a tolerance against the concentration of bioavailable elements in their ecosystem after a sufficient time. However, human activities causing rapid change of concentrations in the environment creates an imminent threat to the adaptation of these organisms.

Elevated concentrations of zinc in water are toxic to many species of algae, and macro-invertebrates such as mollusks and crustaceans (Irwin et al, 1997). Zinc phosphide is highly toxic to freshwater fish including bluegill sunfish and rainbow trout. Zinc toxicity in aquatic environments depends on a number of factors, including water hardness, pH, temperature, and the presence of other contaminants (EPA, 1987). These factors influence the bioavailability of zinc; and therefore, the fraction that can potentially be taken up by organisms. In fresh water, zinc appears to be less toxic at high hardness (EPA, 1987). Moreover, zinc is found to be more acutely toxic to fish at higher temperatures than at lower temperatures (Irwin et al, 1997).

2.2.3 Potential hazards to Humans

Zinc is an essential element in the human diet. It is an important component in the multiplicity of enzymatic reactions and in other beneficial functions (WHO, 2001). Various literature sources indicate that zinc intake in humans should be maintained within an acceptable range. Below this range there is the potential for effects associated with deficiency, and above it, effects associated with toxicity (WHO, 2001). In humans, prolonged excessive dietary intake of zinc can lead to copper deficiency, anemia, and decreased levels of high-density lipoprotein (HDL) cholesterol (TDH, 2003). Other adverse health effects of excess zinc ingestion include pancreas damage, headache, and abdominal pain (Irwin et al, 1997). Inhaling large amounts of zinc, such as zinc dust or fumes from smelting or welding can cause a specific short-term disease called metal fume fever (ATSDR, 1994).

The Recommended Dietary Allowances (RDAs) for zinc are 15 mg/day for men and 12 mg/day for women (ATSDR, 1994). The RDA is an estimate of the zinc needed for growth, development, metabolism and tissue maintenance for over 98% of the healthy American population (IRIS, 1991). On the other hand, the USEPA and the Agency for Toxic Substances and Disease Registry (ATSDR) suggest that a 70-kg adult generally should not regularly consume more than 21 mg zinc per day (TDH, 2003). Harmful health effects generally begin at levels 10-15 times the RDA (in the 100 to 250 mg/day range) (ATSDR, 1994). Eating large amounts of zinc, even for a short time, can cause stomach cramps, nausea, and vomiting. There are no reports on the possible carcinogenicity of zinc and its compounds in humans (IRIS, 1991).

2.2.4 Environmental levels: air, water, and sediment

2.2.4.1 Air

In air, zinc is primarily in the oxidized form, adsorbed to particulate matter. It is found on particles of various sizes, depending on the source of zinc emission (WHO, 2001). The major sources of zinc in air are mining, smelter operations, iron and steel production, waste incineration and coal combustion (ATSDR, 1994).

Zinc particles in the atmosphere are transported to soil and water by wet and dry deposition (WHO, 2001). The mass median diameter for zinc-containing particles in airborne dust is 1.5 μm for rural and urban sites (WHO, 2001). Background atmospheric zinc levels are in the range of 10-300 ng/m^3, with concentrations not exceeding 1000 ng/m^3 for urban industrial areas (WHO, 2001). Wind speed, humidity and acidifying factors cause atmospheric corrosion of metallic zinc, and therefore increase zinc emission to the air.

2.2.4.2 Water

In a publication on Environmental Health Criteria for zinc, the World Health Organization (2001) reported:

> In water, zinc is present primarily in the ionic form, but it has a strong tendency to adsorb to suspended organic matter and clay minerals or to precipitate with iron or manganese oxides, resulting in zinc removal from the water column and enrichment of sediments.

It has to be mentioned that historical zinc concentrations should be viewed with caution due to the possibility of contamination during measurement and analysis of the water quality samples. Older high values of zinc in open ocean waters can be up to three orders of magnitude higher than current values (WHO, 2001). Results from cleaner laboratory analytical methods with lower detection limits show that background zinc concentrations are lower than previously thought (BC Ministry of Environment, 1999)

The total zinc background concentrations of zinc in surface waters are usually less than 50 µg/l (EPA 1980). Concentrations of total zinc in uncontaminated fresh water are typically in the range of 0.5 to 10 µg/l (WHO, 2001). 726 sites from U.S. streams had a median value of 20 µg/l (Irwin et al, 1997). Spear (1981) reported that fresh water concentrations rarely exceed 40µg/l. In clean seawaters, zinc concentrations range from 0.002 to 0.1µg/l and increase with depth (WHO, 2001).

2.2.4.3 Sediment

Zinc adsorbs to organic matter and soil particles, and ultimately precipitates from the water column to enrich the bottom sediments. Natural background concentrations of zinc in typical sediments are approximately 90 mg/kg (USGS, 1999). Sediments having concentrations higher than 200 mg/kg dry weight are classified as "heavily polluted", whereas sediments with zinc concentrations between 90 and 200 mg/kg dry weight, are considered to be moderately polluted (Irwin et al, 1997). In non-polluted sediments, zinc concentrations are typically lower than 90 mg/kg (EPA, 1977).

2.2.5 Bioconcentration, bioaccumulation

Aquatic organisms have evolved efficient mechanisms for accumulation of zinc from water and food (EPA, 1987). The concept of bioaccumulation was originally designed to determine the accumulation of a substance/element in biota in comparison to its occurrence in an environmental compartment, i.e., water, soil or sediment.

Bioconcentration is the net accumulation of a substance by an aquatic organism, as a result of uptake directly from the ambient water through gill membranes or other external body surfaces. The Bioconcentration factor (BCF) is calculated by dividing the "steady state" wet tissue concentration of a particular substance by its "steady state" water concentration. Elevated BCFs may not necessarily cause adverse effects to the health of the organism (WHO, 2001).

Bioaccumulation is a natural process that reflects uptake of a substance by aquatic organisms through all routes (i.e., ambient water and food). The Bioaccumulation factors (BAFs) differ from Bioconcentration factors (BCFs) in that they assume uptake from water and accumulation from the diet (WHO, 2001). For certain chemicals, uptake through the aquatic food chain is the most important route of exposure for wildlife and humans (EPA, 1995). Biomagnification describes the process whereby a chemical, as it is passed through a food chain, reaches increasingly higher concentrations in the tissues of organisms at each higher trophic level (Extoxnet, 1993). It is reported that zinc is not biomagnified (WHO, 2001).

Fish, especially those living in sediments contaminated by zinc, may accumulate zinc directly from the sediments (Irwin et al, 1997). The bioconcentration factor in edible portions of Crassostrea Virginia (adult oyster) is 16,700 (Irwin et al, 1997). In addition, EPA (1987) reported that BCFs derived from laboratory exposures of eastern oysters for 126 days, range from 16,700 to 23,820 in the total soft tissue.

For organic chemicals, baseline Bioaccumulation factors (BAFs) are derived using either field-measured BAFs or by multiplying laboratory-measured Bioconcentration factors (BCFs) by a food-chain multiplier (FCM). For inorganic chemicals such as zinc, BAFs are assumed to equal BCFs (i.e., the FCM is 1.0), unless chemical-specific biomagnification data support using a FCM other than 1 (EPA, 1995).

2.2.6 Interactions with other metals

Zinc in water acts synergistically with copper and ammonia to produce an increased toxic effect on fish (Irwin et al, 1997). In mammals excess zinc can cause copper deficiencies, affect iron metabolism, and interact with the chemical dynamics of lead (Irwin et al, 1997). Zinc can depress copper accumulation in catfish, but simultaneous exposure to copper and zinc can result in enhanced uptake of both metals (Barrera et al, 1995).

Zinc-cadmium interactions diminish negative cadmium effects, and Nickel-zinc interactions have additive toxicity effect to biota (Barrera et al, 1995). Zinc mixture with copper or mercury is additive in toxicity to many aquatic organisms, including oyster larvae (Barrera et al, 1995).

2.3 ENVIRONMENTAL STANDARDS AND CRITERIA FOR ZINC

2.3.1 Texas Water Quality Standards

Water quality criteria of zinc for aquatic life protection are interpreted in terms of the dissolved concentration since it gives a better representation of the bioavailable portion of the metal in the water column. According to Texas Administrative Code (TAC), title 30 (Environmental Quality), Chapter 307 (Texas Surface Water Quality Standards), rule §307.6 (toxic materials), the criteria for zinc in water to protect aquatic life is summarized in Table 2.1 below:

Parameter	Freshwater Acute Criteria µg/L	Freshwater Chronic Criteria µg/L	Saltwater Acute Criteria (µg/L)	Saltwater Chronic Criteria (µg/L)
Dissolved zinc	$0.978we^{(0.8473\ln(hardness))+0.8604)}$	$0.986we^{(0.8473(\ln(hardness))+0.7614)}$	92.7w	84.2w

Table 2.1 Criteria in Water for zinc –Aquatic Life Protection (30 TAC §307.6 toxic materials)

The term *w* is a water-effects ratio, introduced to incorporate the effects of local water chemistry on toxicity. The water-effects ratio is equal to 1 except where sufficient data is available to establish a site-specific, water-effects ratio.

Specific numerical acute aquatic life criteria are applied as 24-hour averages, and specific numerical chronic aquatic life criteria are applied as seven-day averages. Nueces Bay is considered to be a saltwater system, therefore in order to protect aquatic organisms in the bay, The Texas Water Quality standards state that the seven-day average concentration of zinc should not exceed

84.2μg/L, and the 24-hour average concentration should not exceed 92.7 μg/L. There are no toxic criteria for zinc to protect human health for consumption of fish; nonetheless, The Texas Commission on Environmental Quality described criteria for oyster waters in TAC §307.7 as follow:

> Oyster waters should be maintained so that concentrations of toxic materials do not cause edible species of clams, oysters, and mussels to exceed accepted guidelines for the protection of public health. Guidelines are provided by U. S. Food and Drug Administration Action Levels for molluscan shellfish.

2.3.2 Texas Department of Health guidelines for zinc in oyster tissue

Texas Department of Health (TDH) evaluates risks associated with human ingestion of fish containing chemical contaminants, by comparing average contaminant concentrations with health-based assessment comparison (HAC) values (in mg contaminant per kg edible tissue). The health-based assessment comparison value (HAC) is a screening level chosen by TDH to represent concentration in seafood, where adverse health effects are very unlikely to occur. This constant value contains a margin of safety to minimize potential risk to sensitive population such as pregnant or lactating women, children, the elderly and people who consume exceptionally large quantities of fish or shellfish (TDH, 2003).

The calculation of health-based assessment comparison (HAC) values, both for carcinogenic and non-carcinogenic (systemic) effects, are based on a standard body weight of 70 kg and a consumption rate of 30 grams of oysters per day (one 8-ounce meal per week) (TDH, 2001). To evaluate systemic effects, Texas Department of Health uses the U.S Environmental Protection Agency's

(EPA) oral reference dose (Rfd) or the Agency for Toxic Substances and Disease Registry's (ATSDR) chronic oral minimal risk level (MRL). The value of the oral reference dose (Rfd) used is 0.3 mg/kg/day. The same value was established by ATSDR for the minimal risk level (MRL), based on a Lowest Observed Adverse Effect Level (LOAEL) of 1 mg/kg/day. The body weight of 70 kg is multiplied by the Rfd value of zinc (0.3 mg/kg/day) to obtain the acceptable zinc intake for a person, which is 21 mg/day. This value is divided by the consumption rate of 30 g oysters per day to derive the health-based assessment comparison (HAC) value for zinc in oysters, which is 700-mg/kg edible tissue. In other words, in order to protect public health from unacceptable exposure to oysters from Nueces Bay, the average zinc concentration in oysters from the bay should be consistently below 700-mg/kg edible tissue.

2.3.3 EPA screening levels and criteria

Sediments are an integral part of the aquatic environment in where they serve as a reservoir and a source of contaminants to the water column (Jones et al, 1997). To determine whether sediment quality is acceptable, site-specific data of sediment concentrations can be compared with sediment screening values or benchmarks for the contaminant in concern.

Various methods have been studied to develop sediment quality guidelines. Among these, are integrative benchmarks developed by the National Oceanic and Atmospheric Administration (NOAA) and the Florida Department of Environmental Protection (FDEP) for marine and estuarine sediments. The NOAA and FDEP values were developed from data from several investigations throughout the United States, which used different approaches to evaluate sediment quality (e.g., toxicity tests, EqP, AET) (Jones et al, 1997).

The National Oceanic and Atmospheric Administration (NOAA) use benchmarks developed by Long et al (1995). These sediment benchmarks are:

- The Effects Range–Low (ER–L): Level below which contaminants in sediment are not likely to have adverse effects on animals that live in sediment.
- Effects Range–Median (ER–M): Level above which contaminants in sediment probably have adverse effects on animals that live in sediment.

The Florida Department of Environmental Protection (FDEP) uses an approach developed by MacDonald et al. (1994) that is similar to the NOAA approach. The FDEP benchmarks are the threshold effects level (TEL) and probable effects level (PEL). The TEL represents the upper limit of the range of sediment contaminant concentrations dominated by no effects data, whereas the PEL represents the lower limit of the range of contaminant concentrations that are usually or always associated with adverse biological effects (Jones et al, 1997).

For the chemical zinc, sediment quality benchmarks for marine and estuarine sediments are shown below:

- NOAA

  ER-L = 150 mg/kg dry weight

  ER-M = 410 mg/kg dry weight

- FDEP

  TEL = 124 mg/kg dry weight

  PEL = 271 mg/kg dry weight

2.4 PREVIOUS STUDIES

On April 1976, an intensive monitoring survey of Nueces Bay (Jensen et al, 1977) was undertaken. Five permitted dischargers to the bay system were inventoried: municipal sewage treatment facilities at the city of Portland, privately owned sewage treatment facilities at the Ramada Inn, Centex Cement Corporation, Central Power & Light Company, and PPG Industries. The discharge from the Centex Cement Corporation has ceased subsequent to this survey. Field data collected during the survey indicated good water quality conditions in Nueces Bay. No violations of Texas surface water quality standards for Nueces Bay were found at that time. Nonetheless, high concentrations of cadmium and zinc were detected in oyster tissue collected from Nueces Bay .

In 1982, the Texas Department of Water Resources (TDWR) conducted a special study (Bowman et al, 1985) of the Corpus Christi Inner Harbor, where several samples of heavy metals in waters were collected in different stations of the harbor. Arsenic was reported to be present in most samples, but not excessive. Zinc concentrations found in sediments of the Inner Harbor were exceptionally high, up to 2100 mg/kg in one station (Bowman et al, 1985). The study also reported an improvement of water quality in the Corpus Christi Inner Harbor since 1973, attributed to reduced loading to the harbor from wastewater sources, and removal of some of its contaminated bottom sediments after dredging.

In another study (Barrera et al, 1995), the U.S. Fish & Wildlife Service conducted baseline contaminants assessments of sediments and biota from the Corpus Christi Bay Complex for the period 1988-1989. Chemical analyses were obtained for 9 biota samples and 18 sediment samples from Nueces Bay, and for 3 biota samples and 7 sediment samples from the Inner Harbor. As a result of this study, oysters from both Nueces Bay and the Inner Harbor had extremely elevated levels of zinc. Nueces Bay oysters had a Geometric Mean (GM) of 6006 ppm dw, whereas Inner Harbor oysters had a GM of 11600 ppm dw (Barrera et al, 1995). Zinc was also elevated in hardhead catfish of Nueces Bay, the Nueces River, and the Inner Harbor. Zinc contamination as well as that of cadmium and copper in the Inner Harbor, was reported to have originated from the operation of a zinc smelting facility, which ceased operation in the early 1980's. In fact, Barrera et al (1995) reported in their study:

> Historically, discharges from chemical and petrochemical facilities, as well as spills from shipping transfer activities, have been sources for the deposition of heavy metals and organic pollutants in sediments of the Inner Harbor. One notable example was the pollution of the Inner Harbor with zinc as a result of the operation of a smelting facility for thirty-five years. Several billion tons of zinc were processed during that time and Inner Harbor waters and sediments still remain heavily contaminated.

In a recent study by Ward et al (1997), data was compiled to assess water, sediment, and tissue quality of Corpus Christi Bay, and evaluate their trends over time. Nueces Bay had the highest mean tissue concentrations in the study area for cadmium, copper, lead and zinc. Also, the highest total suspended solids (TSS) concentrations were found in Nueces Bay. PCB and PAH concentrations were also high in the Inner Harbor. The trend through time for metals concentrations in the Inner Harbor was determined to be declining due to advanced waste treatment and dredging activities. One of the hypotheses presented in this study, to partially explain the elevated metals in Nueces Bay, was that they might be due to the influx of water (and suspended sediments) from the Inner Harbor through the CP&L generating station. From a sediment Quality Triad (SQT) study, conducted by Carr et al (1998) in the Corpus Christi Bay study area, sediment samples from sites in Nueces Bay exceeded the threshold-effects level (TEL) or the effect range low values for zinc, cadmium and mercury. Values for zinc in sediments from this study are shown in Appendix E.

Chapter 3: Data description and analysis

3.1 ZINC MONITORING DATA

The data analyzed in this project were mainly drawn from the monitoring program database operated by the Texas Commission on Environmental Quality (TCEQ). These sets of data comprise measurements of some of the water and sediment zinc concentrations within the Nueces Bay study area, and the adjacent Inner Harbor channel. For the tissue data, measurements of zinc concentrations in oyster tissue were obtained from the Texas Department of Health (TDH).

The water and sediment quality data is generally sparse and discontinuously distributed in space and time. The interpretation of this data makes it difficult to confirm trends or relation to pollution sources to the bay system. The analysis of the data comprised a comparison of zinc contamination levels with background or other screening levels. Concentrations that are not higher than background are supposed to be non-hazardous (Jones at al, 1997).

The TCEQ database uses the STORET code system to organize water and sediment quality monitoring parameters. For zinc monitoring data, the STORET code numbers are:

01090: Dissolved zinc in μg/l

01092: Total zinc in μg/l

01093: zinc in sediment (mud, bottom deposits) in mg/kg dry weight.

Collection techniques and sampling procedure used by TCEQ for total and dissolved metals in water are fully explained in Appendix G.

An inventory of the TCEQ monitoring stations in the study area, where water and sediment quality data are available, was made. The number of monitoring stations used in both Nueces Bay and the Inner Harbor are 6 and 13, respectively. Figure 3.1 presents a map showing the station numbers and locations of these monitoring locations.

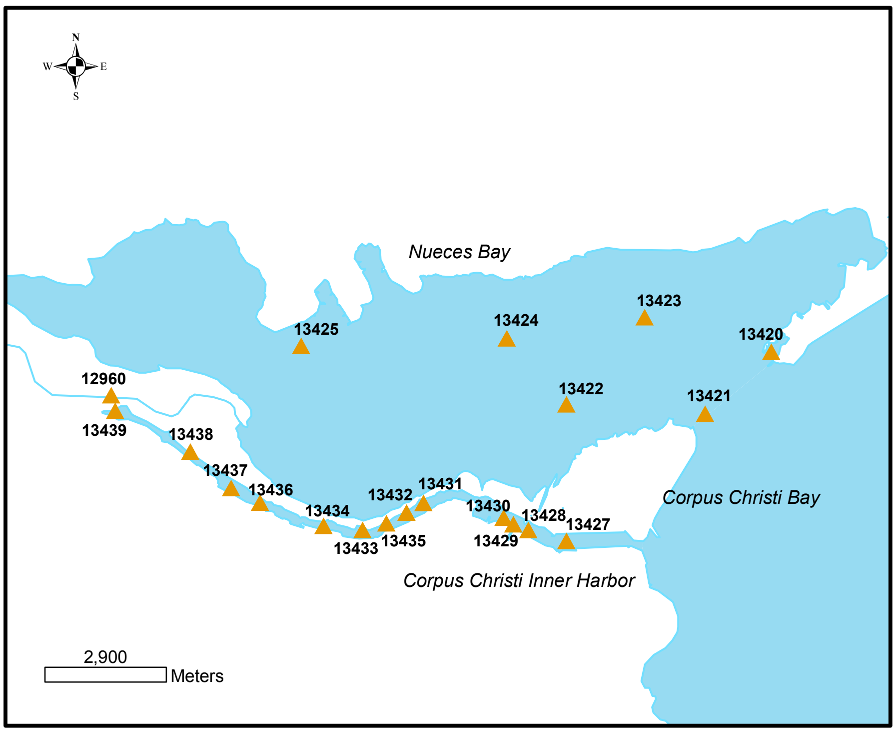


Figure 3.1 Location of TCEQ monitoring stations in Nueces Bay & Inner Harbor

3.1.1 Zinc in water

When interpreting the data on water concentration of zinc, it is necessary to be aware that the higher values reported in early studies might be due to contamination of the samples. It is reported that contamination leading to levels as high as 20 μg/l is quite possible during sampling and filtration of waters (WHO, 2001). Ultra clean methods of sampling, using containers that are carefully selected and pre-cleaned, may reveal zinc concentrations in open ocean waters, between 1 to 3 orders of magnitude higher than current values (WHO, 2001).

TCEQ data for total zinc concentration in water (Table 3.1) are available at only four monitoring stations within Nueces Bay.

Station	Date	Total zinc (μg/L)
13420	8/8/1983	45
13421	8/8/1983	15.0
13422	7/16/1974	100.0
	1/5/1977	170.0
	9/24/1980	48.0
	8/13/1981	5.0
	8/26/1982	19.0
	5/27/1983	20.0
	8/8/1983	84.0
	6/25/1984	26.0
	8/6/1985	73.0
	5/29/1986	139.0
	5/13/1987	70.0
	5/27/1988	20.0
13423	8/8/1983	44.0

Table 3.1 Total zinc in water for stations in Nueces Bay [Source: TCEQ]

Three out of four monitoring stations report one measurement only of total zinc, made in 1983. In addition, there are no total zinc measurements available after 1988. Prior to 1980, total zinc concentrations measured in station 13422 were significantly higher than those reported after that year, except for one measurement in 1986. This might be due to historical contamination of the area caused by the operation of the ASARCO smelting facility. In addition, dredging activities in the Inner Harbor at that time, may have reduced bottom sediments rich in zinc, and thus improved the quality of water exchanged between the Inner Harbor and Nueces Bay through the Central Power and Light (CP&L) station. Measurements reported between 1980 and 1988 are plotted in Figure 3.2, and give an average total zinc concentration of 46.8 µg/l. In general, the total zinc data are sparse, and insufficient to determine a consistent trend.

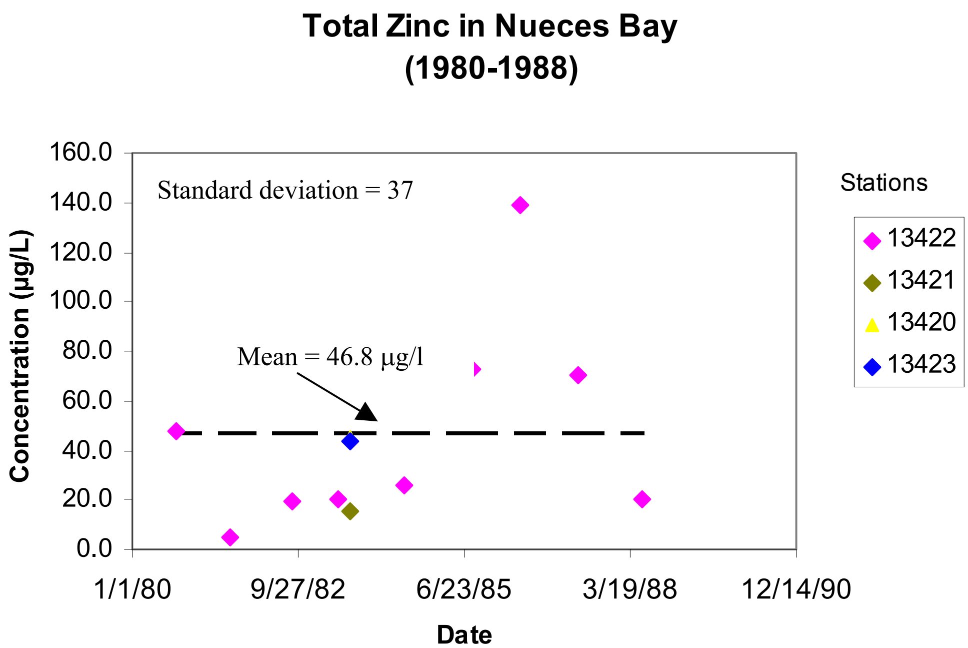


Figure 3.2 Total zinc in water in Nueces Bay [data source: TCEQ]

According to Eisler (1993), background concentrations of zinc rarely exceed 40 µg/l in water. Moreover, in clean seawaters, zinc concentration normally range from 0.002 to 0.1µg/l (WHO, 2001). Average concentrations of total zinc in Nueces Bay waters exceed the background levels.

For the Inner Harbor, Total zinc concentrations obtained from TCEQ are available in monitoring stations for the period 1974-2001, and is summarized in Appendix A. A plot of this data for the period 1980-2001 is shown in Figure 3.3, and gives an average concentration of total zinc in the Inner Harbor of 37μg/l.

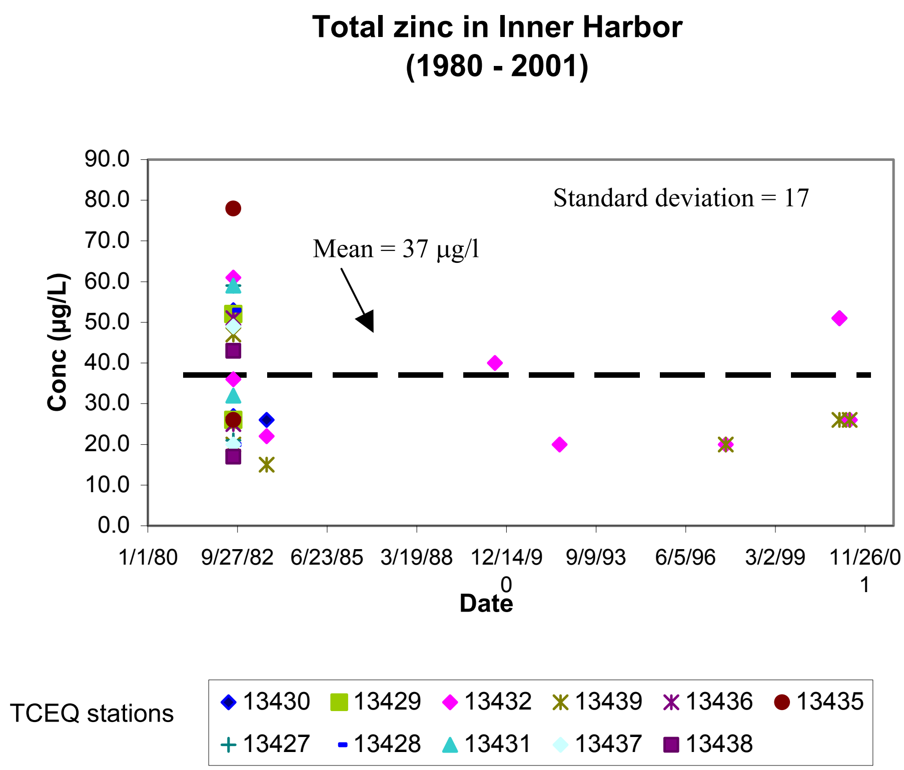


Figure 3.3 Total zinc in Inner Harbor for the period 1980-2001 [data source: TCEQ]

To compare total zinc levels of Nueces Bay with those of the Corpus Christi Inner Harbor, a map showing the spatial distribution of average concentrations within each monitoring station was developed (Figure 3.4). The averaging period for stations in Nueces Bay is 1974-1988, and that of the Inner Harbor is 1974-2001. For detailed information on total zinc data in the Inner Harbor, see Appendix A. As shown in the map, total zinc levels are comparable between Nueces Bay and the Inner Harbor, with the highest concentrations reported in the Inner Harbor. Hydrodynamic circulation in Nueces Bay and water exchange between Nueces Bay, Corpus Christi bay and Inner Harbor might explain the quite similar values of total zinc in water between Nueces Bay and the Inner Harbor.

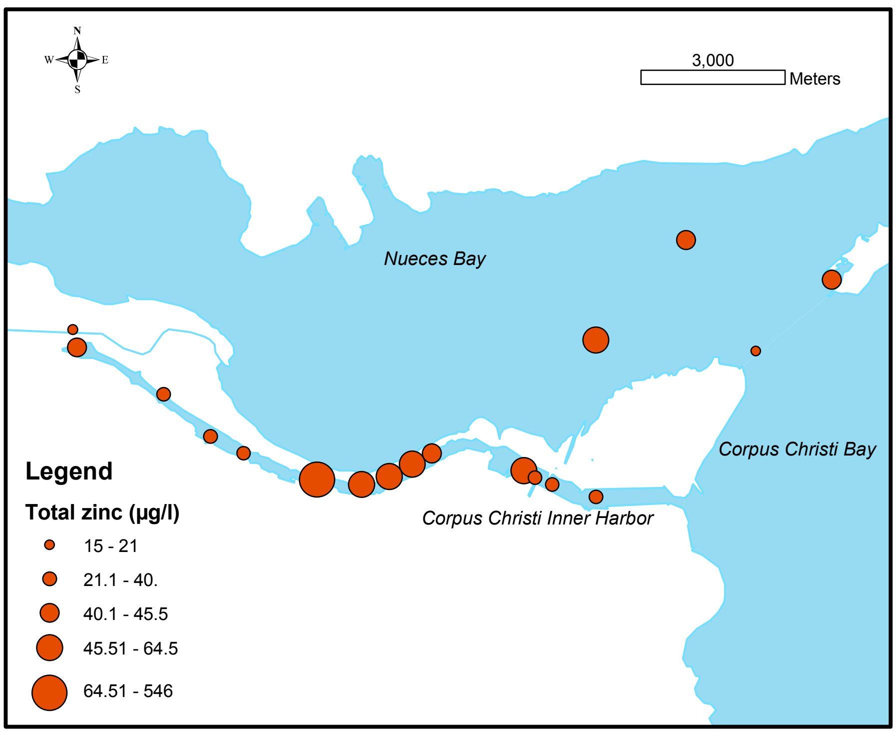


Figure 3.4 Average concentrations of total zinc in water (µg/l) in monitoring stations within Nueces Bay and Inner Harbor.

For the dissolved fraction of zinc in water, data from TCEQ database system was available for only one monitoring station (Table 3.2). The average dissolved zinc in this station (12.2 μg/l) is almost ¼ of the average total zinc in Nueces Bay (46.8μg/l). The Corpus Christi Bay National Estuary Program (CCBNEP), using ultra clean method to avoid contamination during sampling, collected additional dissolved zinc data (Table 3.3). Site Locations of the stations in table 3.3 are given in Appendix B.

Station	Date	Dissolved zinc (μg/L)
13425	2/25/1999	9
	10/3/2000	16
	1/24/2001	12
	5/10/2001	8
	7/24/2001	16

Table 3.2 Dissolved zinc in Nueces Bay, by conventional method [source: TCEQ]

Station	Date	Dissolved zinc (μg/L)
15	4/19/2000	5.81
	8/27/2000	1.70
	10/23/2000	4.81
	3/14/2001	4.01
16	4/19/2000	2.83
	8/27/2000	3.29
	10/23/2000	2.91
	3/14/2001	1.78
19	4/19/2000	8.08
	8/27/2000	4.00
	10/23/2000	4.99
	3/14/2001	5.94

Table 3.3 Dissolved zinc in Nueces Bay, by ultra-clean method [source: CCBNEP]

Both dissolved zinc data, using the conventional method and ultra-clean method of sampling are plotted in a graph (Figure 3.5) to show the difference between average measurements of all stations done within the same period. The average concentration of dissolved zinc measured with the conventional sampling method (12.2 µg/l) is 3 times higher than the one measured with the clean method (4.18 µg/l). Therefore, an effort should be made to conduct ultra clean measurements of zinc, in case new values of total zinc with the clean method might reveal concentrations within background levels or consistently lower than the current values.

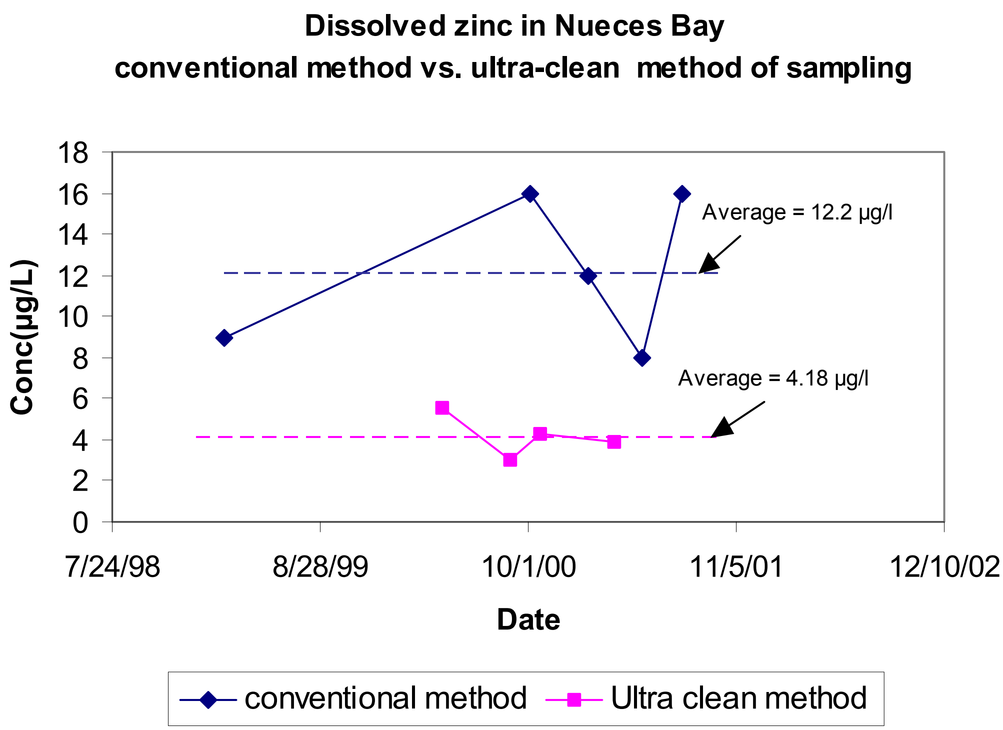


Figure 3.5 Dissolved zinc in Nueces Bay using the conventional method and the ultra-clean method of sampling

Considering Nueces Bay as a saltwater system, dissolved zinc concentrations in the bay are everywhere below the acute criteria (92.7 µg/l) and chronic criteria (84.2µg/l) for the protection of aquatic life as dictated in the Texas Surface Water Quality Standards (TAC §307.6).

3.1.2 Zinc in sediments

The Texas Commission on Environmental Quality (TCEQ) has historical data of zinc concentrations in sediments (mg/kg dry wt) in 6 stations within Nueces Bay. The TCEQ monitoring data (Table 3.4) extends from 1973 to 2002. The average concentration of zinc in sediments of Nueces Bay is 102 mg/kg for the period 1973-2002, and 100.4 mg/kg for the period 1980-2002.

Other sources of sediment zinc quality data include measurements conducted from October 24th to 28th 1997 by Carr, Montagna, and Kennicutt II (1998) in the study: *Sediment Quality Assessment of Storm Water Outfalls and other selected sites in the Corpus Christi Bay National Estuary program* Study Area. The Nueces Bay data related to this source are shown in Table 3.5, while location of sampling stations and zinc data for other site locations are given in appendix E.

In addition, The Corpus Christi Bay National Estuary Program (CCBNEP) collected some zinc sediment data from Nueces Bay in March 2001 (Table 3.6), and found an average concentrations of 37 mg/kg dry weight. Site locations for these stations are shown in Appendix B.

Station	Date	Zinc in sediment (mg/kg dry wt)
13420	4/12/1976	117.0
	7/22/1986	56.0
13421	4/12/1976	48.0
	5/29/1986	170.0
	7/7/1998	55.0
	7/11/2000	30.0
	1/24/2001	71.0
	2/19/2002	118.0
13422	10/15/1973	230.0
	1/17/1975	77.0
	4/12/1976	112.0
	1/5/1977	33.0
	12/30/1977	240.0
	9/24/1980	180.0
	8/13/1981	210.0
	5/27/1983	37.0
	6/25/1984	250.0
	8/6/1985	150.0
	5/29/1986	137.0
	5/13/1987	156.0
	5/27/1988	130.0
	3/15/1995	24.0
	7/7/1998	42.0
	7/19/1999	30.0
	7/11/2000	32.0
	1/24/2001	56.0
	2/19/2002	106.0
13423	4/12/1976	34.0
	3/15/1995	109.0
13424	3/15/1995	71.0
13425	3/15/1995	72.0
	7/7/1998	103.0
	7/19/1999	77.0
	7/11/2000	78.0
	1/24/2001	77.0
	5/10/2001	104.0
	2/19/2002	168.0
	5/16/2002	113.0

Table 3.4 Zinc in sediments in Nueces Bay [data source: TCEQ]

Station	Date	Zinc in sediment (mg/kg dry wt)
1	Oct 97	99.81
2	Oct 97	32.01
R1	Oct 97	146.45
R2	Oct 97	134.07

Table 3.5 Zinc in sediments in Nueces Bay from Carr et al (1998)

Station	Date	Zinc in sediment (mg/kg dry wt)
15	3/14/2001	25.14
16	3/14/2001	31.26
19	3/14/2001	53.12

Table 3.6 Zinc in sediments in Nueces Bay [data source: CCBNEP]

A plot of zinc concentrations in sediments of Nueces Bay is shown in Figure 3.6. This graph includes measurements from several stations in the bay that were obtained from the 3 different sources: TCEQ, CCBNEP and Carr et al (1998). The mean concentration of zinc in Nueces Bay sediments, accounting for all available data in the period 1980-2002, is 95.5-mg/kg dry weight. This mean concentration slightly exceeds the background zinc concentration of 90 mg/kg established by EPA (1977).

A comparison of this sediment data with sediment quality benchmarks shows 13 samples exceeding the Florida Department of Environmental Protection (FDEP) Threshold Effects Level (TEL), and 8 samples exceeding the National Oceanic and Atmospheric Administration (NOAA) effects Range–Low (ER–L). In non-polluted sediments, zinc concentrations are typically lower than 90 mg/kg (EPA, 1977).

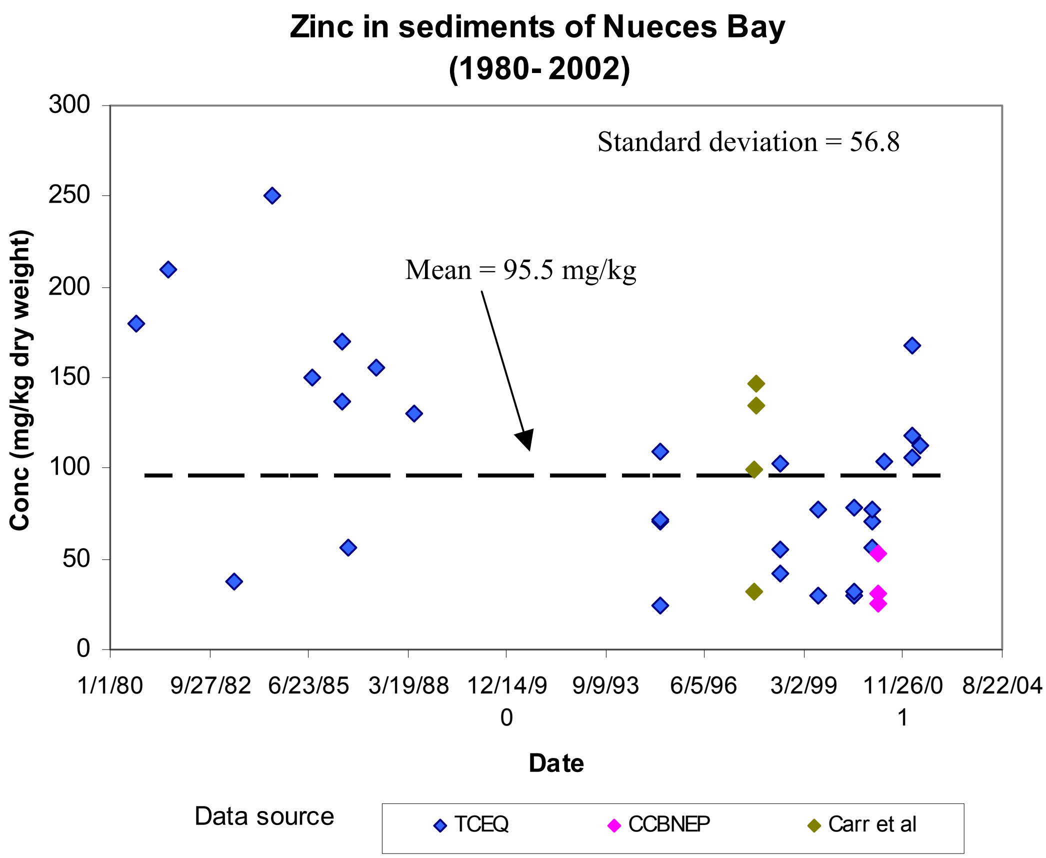


Figure 3.6 Concentrations of zinc in Nueces Bay sediments (1980-2002) from 3 different data sources: TCEQ, CCBNEP and Carr et al (1998).

The Inner Harbor sediments were heavily contaminated by zinc prior to 1980, with concentrations exceeding 5000 mg/kg dry wt in some stations, but the general trend is decreasing concentrations, probably due to dredging activities in the Inner Harbor ship channel. Available data for zinc in the Inner Harbor's sediments are given in Appendix D. A graph of zinc concentrations in Inner Harbor sediments for the period 1980-2002 is given in Figure 3.7. The average zinc concentration in sediments of the Inner Harbor is around 497 mg/kg for the period 1980-2002.

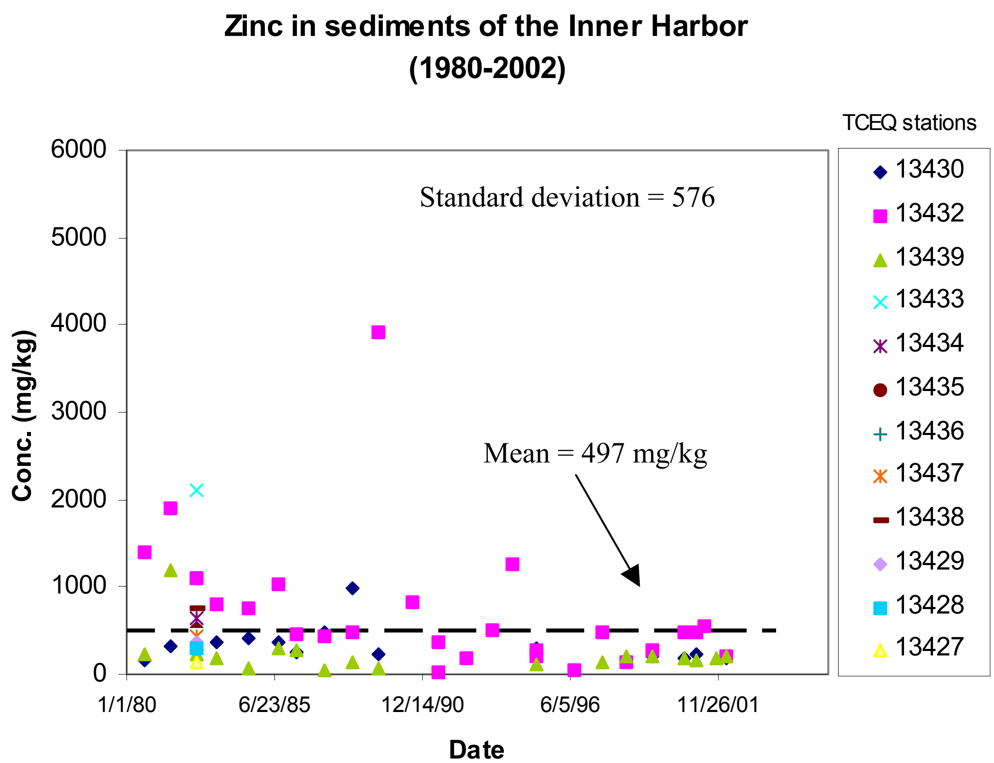


Figure 3.7 Zinc concentrations in Inner Harbor sediments for the period 1980-2002 [Data source: TCEQ]

Figure 3.8 displays a map showing the range of average zinc concentrations in sediments for each TCEQ monitoring station in Nueces Bay and the in the Corpus Christi Inner Harbor, during the period 1973-2002. The measurements available in TCEQ monitoring stations indicate some concentrations in the Inner Harbor that are more than one order of magnitude higher than those in Nueces Bay.

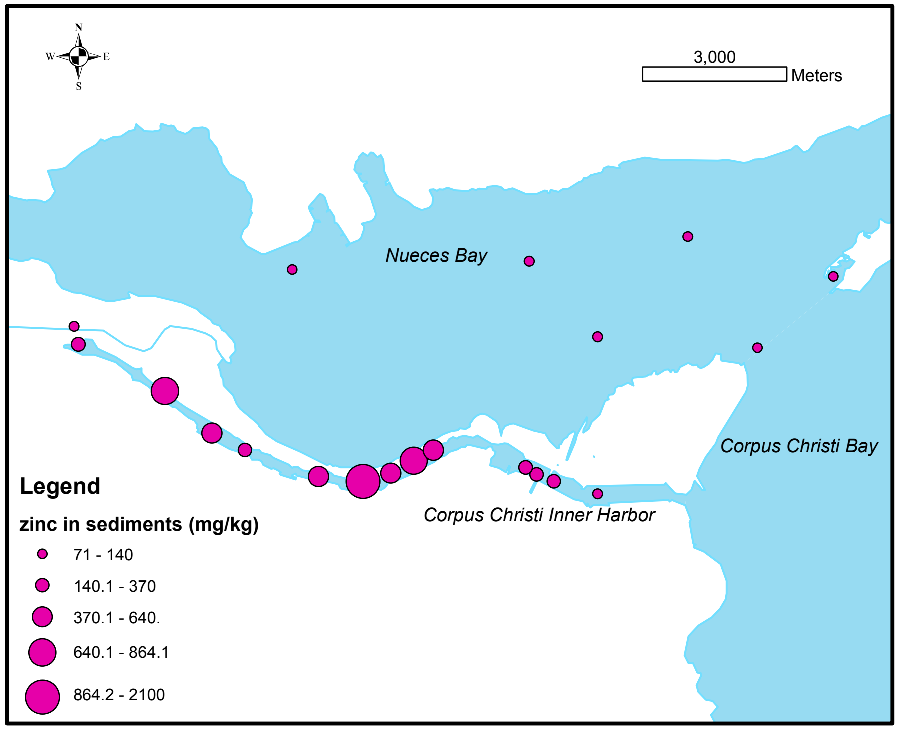


Figure 3.8 Average concentrations of zinc in sediments (mg/kg) in monitoring stations within Nueces Bay and Inner Harbor.

A graph showing the correlation between average concentrations of zinc in sediment and total zinc in water for Nueces Bay and Inner harbor for the period 1973-2002 is plotted in Figure 3.9. The data points are scattered and the correlation factor between the two dataset is as low as 0.1 (Figure 3.9), which indicates that there is no obvious relationship between zinc in sediment and zinc in water.

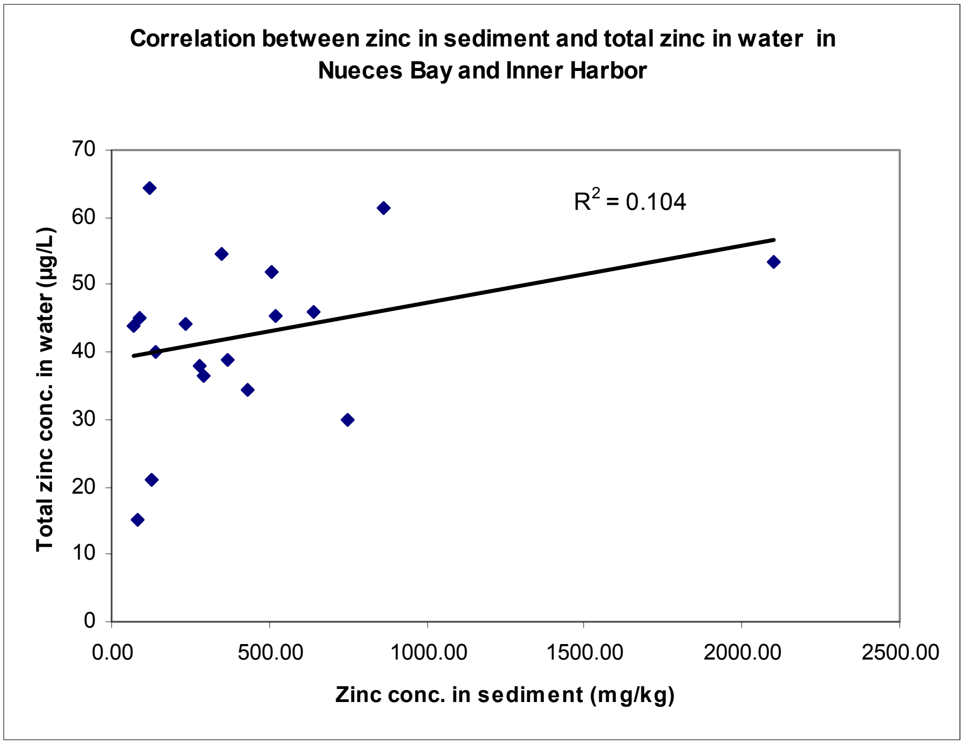


Figure 3.9 Graph showing relationship between zinc in sediment and total zinc in water for Nueces Bay and Inner Harbor

3.1.3 Zinc in oyster tissue

The Seafood Safety Division of Texas Department of Health (TDH) collected a total of nineteen oyster samples from six sites within Nueces Bay between 1980 and 2002. The latest samples were collected in February, July and August 2002. Four sites have known longitude and latitude coordinates: the Nueces Causeway site, a point near the Central Power and Light (CPL) cooling water outfall (CPL site), Land tract #752 north of US 181 highway, and land tract # 723 in the center of Nueces Bay. The enclosed map of Nueces Bay (Figure 3.10) shows these sample collection sites.

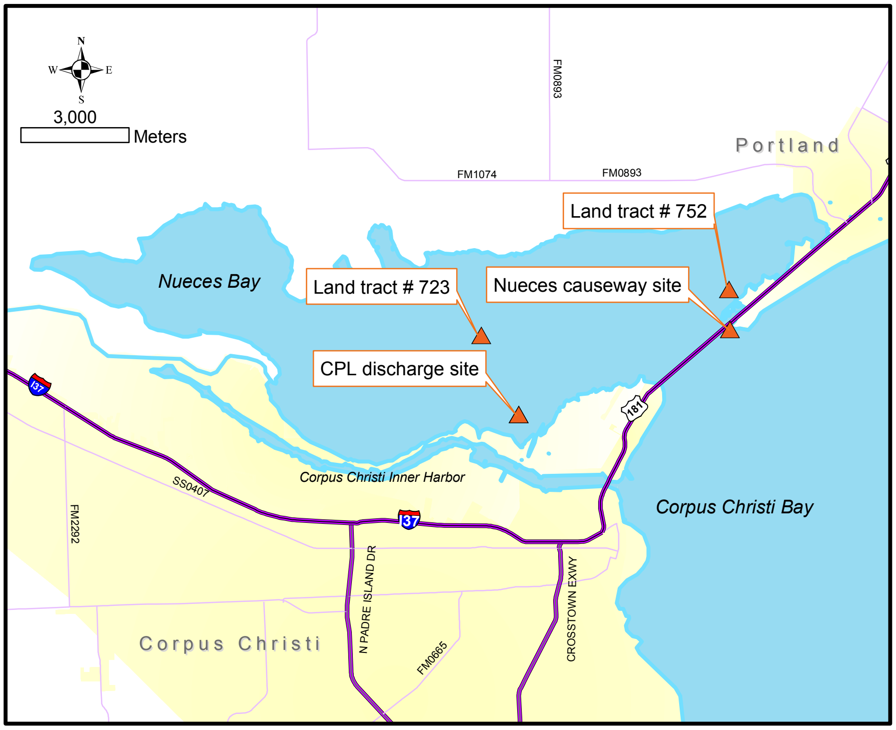


Figure 3.10 Site location of oyster tissue sampling in Nueces Bay

The index levels (ppm) or concentrations of zinc in oyster tissue (mg/kg edible tissue) found in all of the 6 sampling locations are given in Table 3.7, along with collection dates and oysters lengths (in inch). A 3D representation of the number of oyster samples and zinc index level in function of time is shown in Figure 3.11.

In all samples, zinc in oysters from Nueces Bay exceeded the Health-based assessment comparison value (HAC) of 700 mg/kg. Between 1980 and 2002, oyster zinc concentrations were in the range 704 - 2483 ppm, and averaged 1395 mg/kg (ppm).

Sampling Station	Date	Length (inches)	Index Level (mg/kg edible tissue)
Land Tract #723	5/5/1980	10-4	1300
	5/5/1980	10-4	1400
	5/5/1980	10-4	1800
	5/5/1980	12-4	1700
	9/23/1982	ND	1220
	9/23/1982	ND	1190
Land Tract #708A	3/10/1983	ND	930
	3/10/1983	ND	1400
	8/17/1994	2-3	2482.66
ND	7/12/1984	ND	1670
	7/12/1984	ND	1660
Land Tract #752	8/17/1994	3	2293.99
Causeway site	2/19/2002	2.5-3.0	704
	2/19/2002	2.5-3.0	710
	2/19/2002	2.5-3.0	903
CPL site	2/21/2002	3	1450
	2/21/2002	3	1140
	2/21/2002	3	1320
	2/21/2002	3	1220

Table 3.7 Zinc in Nueces Bay oyster tissue [source: TDH]

The 1994 samples were taken from the vicinity of Rincon Point, east of the 2002 site nearest the CP&L site (TDH, 2003). These samples show the highest zinc levels in oysters. (Range: 2294-2482 ppm), and were the reason why TDH closed Nueces Bay to the harvesting of oysters.

The 2002 oysters samples were collected from two sites: the Nueces Bay causeway site, and the Central Power and Light (CPL) discharge site. Average zinc in oysters from the site near CP&L station is 1486 mg/kg, while the average from the causeway site is 770 mg zinc/kg edible tissue.

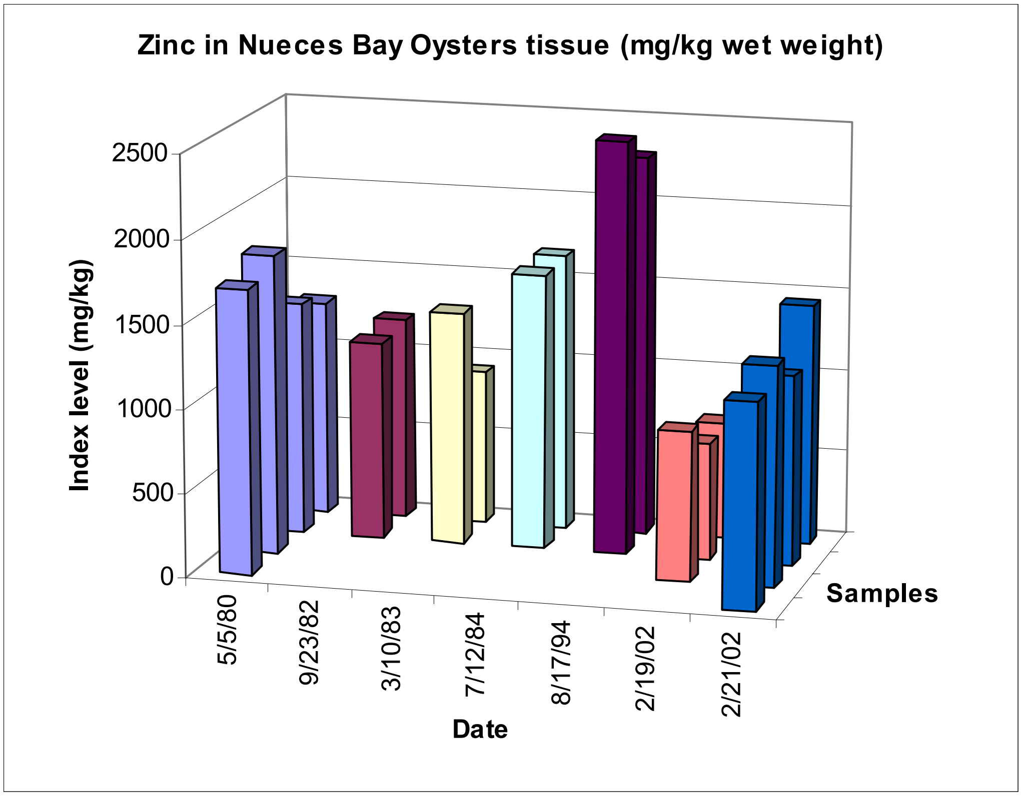


Figure 3.11 Temporal distribution of zinc in Nueces Bay oyster tissue

3.2 GIS DATA

3.2.1 Map projection

Map projections transform the surface of the earth or a portion of the earth onto a flat surface. This two-dimensional representation always results in some distortions of shape, distance, direction, scale, and area. Some projections minimize distortions in some of these properties at the expense of maximizing errors in others, whereas other projections are attempts to only moderately distort all of these properties.

A standard map projection of all data sources is needed to ensure a compatible display of layers in ArcGIS. Spatial digital data for this project come from different sources and thus is usually found in various map scales and coordinate systems. The map projection used for this study is The Texas Centric Mapping system (TCMS) in Albers Equal Area conic projection. The TCMS is among the commonly used map projections for the state of Texas, and its use has become encouraged for data deliverables for state funded projects. Parameters of TCMS are shown in Table 3.8.

Projection	Albers Equal Area Conic
Spheroid	GRS 80
Datum	North American Datum of 1983 (NAD83)
Longitude of Origin	100 degrees West (-100)
Latitude of Origin	18 degrees North (18)
Standard Parallel #1	27 degrees 30 minutes (27.5)
Standard Parallel #2	35 degrees (35)
False Easting	1,500,000 meters
False Northing	6,000,000 meters
Units of Measure	Meters

Table 3.8 TCMS projection parameters

Projection of digital data in the GIS environment is done using ArcToolbox from the ArcGIS software.

3.2.2 TCEQ Water Quality Segments

The Texas Commission on Environmental Quality has individually defined streams and waterbodies for the State of Texas as listed in *Title 30, Chapter 307 of the Texas Administrative Code (TAC)*, also known as the Surface Water Quality Standards. These TCEQ water quality segments are assigned unique identification numbers. They are intended to have relatively homogeneous chemical, physical, and hydrological characteristics, to provide a basic unit for assigning site-specific standards and for applying water quality management programs of the agency.

The TCEQ water quality segments layer can be obtained from the TCEQ website. It is available online in a GIS shapefile format from the web link: **http://www.tnrcc.state.tx.us/gis/hydro.html**

The segments layer shows the classified and unclassified stream segments for the state. Classified segments also referred to as designated segments, refer to water bodies that are protected by site- specific criteria. The classified segments are listed and described in Appendix A and C of Chapter 307.10 of the Texas Administrative Code. Classified waters include most rivers and their major tributaries, major reservoirs, and estuaries. Unclassified waters are those smaller water bodies that do not have site-specific water quality standards assigned to them, but instead are protected by general standards that apply to all surface waters in the state.

The water quality management segment data layer obtained from TCEQ is in the Texas State Mapping system (TSMS) Lambert projection. The stream segments data is projected to Texas Centric Mapping system (TCMS). Figure 3.12

shows the TCEQ segments and their boundaries of streams and waterbodies in the study area. Nueces Bay is designated as Segment 2482, whereas the Corpus Christi Inner Harbor is called Segment 2484. The two segments of Nueces River upstream of the Nueces Bay, namely the Tidal portion and the portion below Lake Corpus Christi are respectively called Segment 2101 and Segment 2102.

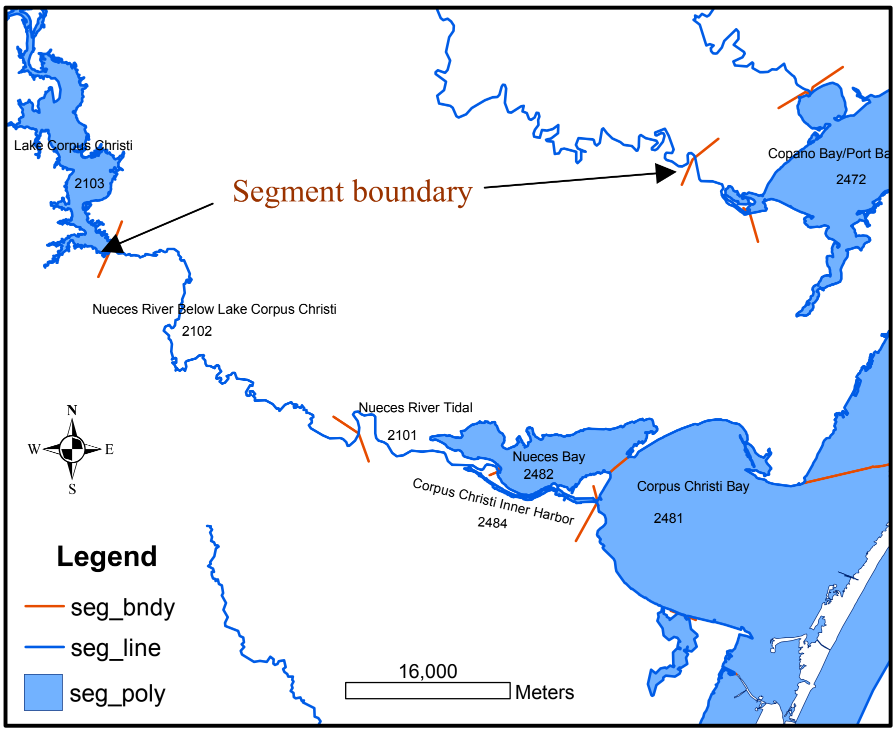


Figure 3.12 TCEQ Water Quality stream and waterbody segments

3.2.3 Hydrologic Unit Codes (HUC)

Hydrologic Unit Codes (HUC) boundaries are a subdivision of the Unites States into successively smaller hydrologic units, made by the United States Geological Survey (USGS), to show major and minor river basins. These subdivisions are classified into four levels: regions, sub-regions, accounting units, and cataloging units.

The hydrologic units are arranged within each other, from the smallest (cataloging units) to the largest (regions). Each hydrologic unit is identified by a unique hydrologic unit code (HUC) consisting of two to eight digits based on the four levels of classification in the hydrologic unit system. An eight-digit code uniquely identifies each of the four levels of classification within four two-digit fields. The first two digits identify the water-resources region; the first four digits identify the sub-region; the first six digits identify the accounting unit, and the addition of two more digits for the cataloging unit completes the eight-digit code.

The HUC coverage file for the state of Texas was obtained from a database established at CRWR. After projecting the file from Lambert Conformal Conic to TCMS projection system, 9 HUC polygons around the Nueces Bay area were initially selected to reduce the coverage to a smaller study area. This was done using “export data” in Arc Map to export the selected features to a shapefile.

Figure 3.13 displays a large area surrounding Nueces Bay, covering 9 Hydrologic Unit codes. Three of these Hydrologic units, namely 12110111, 12110201, and 12110202 are used to further delimit the study area for watershed delineation.

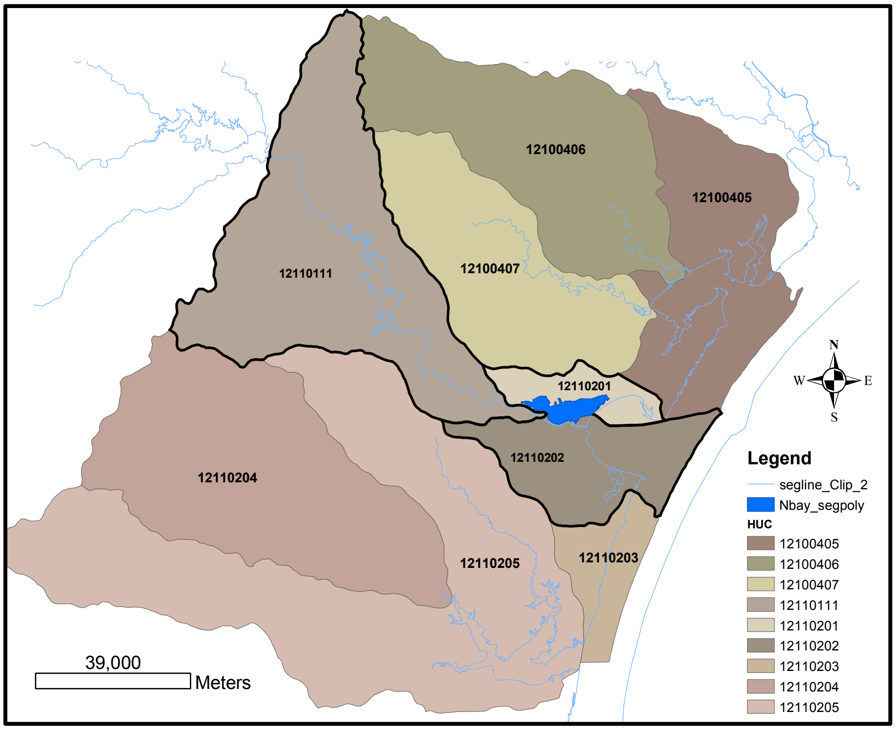


Figure 3.13 Hydrologic Unit Code Boundaries within Nueces Bay area

3.2.4 Digital Elevation Models

Digital Elevation Models are digital records of terrain elevations for ground positions at regularly spaced horizontal intervals. These grids are derived from standard topographic quadrangle maps through the use of hypsographic data and /or photogrammetric methods.

The Digital Elevation models of the study area are obtained from tiles of The National Elevation Dataset (NED). The NED is a raster product assembled by the U.S. Geological Survey (USGS) and designed to provide national elevation data in a seamless form. It has a resolution of 1 arc-second (approximately 30 meters).

The data is in decimal meters, and has a geographic projection with North American Datum 1983. The NED is retrieved in the form of tiles, in which each tile name represents the (x, y) coordinates of the upper left corner of the tile. The NED files are in Arcgrid format, and elevation information is given in the form of floating point decimal data in meters.

Hydrologic units (HUC) covering and surrounding the area of study are used to determine which NED tiles need to be extracted. The study area is initiated on 3 hydrologic units surrounding Nueces Bay. These Hydrologic units are: 12110111, 12110201, and 12110202. The polygon features of the 3 Hydrologic units are selected and exported as a shapefile in ArcMap and called *Nueces_HUC*. This polygon *Nueces_HUC* is then projected to geographic coordinate system to be displayed over the DEM tiles. 4 NED tiles are used for the study area, namely: dem9828, dem9829, dem9928, and dem9929. The spatial extent of this DEM coverage, as shown in Figure 3.14, covers the extent of the hydrologic units around the Nueces Bay area.

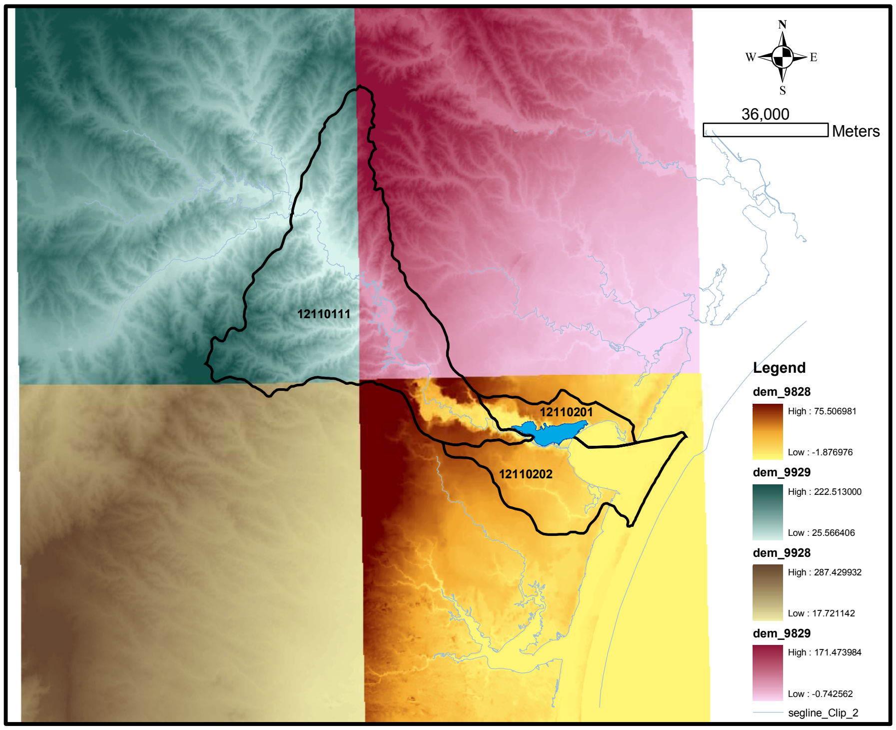


Figure 3.14 NED tiles covering the HUCs around Nueces Bay

The 4 DEM tiles were then merged together using the following commands in ArcInfo Workstation:

Grid: elev = merge (DEM9828, DEM9829, DEM9928, DEM9929)

The resulting merged DEM grid *elev* is next projected to TCMS coordinate system along with the *Nueces_HUC* polygon using the projection commands in ArcToolbox.

The projected Dem grid is called *prj_ele*. *Nueces_HUC* polygon outline is then buffered by 10 kilometers to incorporate the surrounding drainage features that may influence drainage paths within the study area. This buffered outline was used to clip the DEM to a smaller extent, resulting in *clipdem*. The buffer and clipping tasks are carried out in ArcInfo Workstation:

```
Arc: shapearc Nueces_HUC Nueces_HUC
Arc: build Nueces_HUC
Arc: buffer Nueces_HUC buffer # # 10000 #
Arc: grid
Grid: setwindow buffer buffer
Grid: setcell 30
Crid: clipdem = selectpolygon (prj_elev, buffer, inside)
```

The study area outline, buffer and DEM are shown in Figure 3.15. The stream segments were also clipped to the *Nueces_HUC* polygon using the “Clip” function in ArcGIS. The Clip function is found in the “Geoprocessing Wizard” tool and is used to cut out a piece of one layer using one or more of the polygons in another layer. The clipped shapefiles of TCEQ line and polygon segments are named *Tnrcc_seg_line* and *Tnrcc_seg_poly* respectively. Figure 3.16 shows the resulting clipped DEM and TCEQ segments.

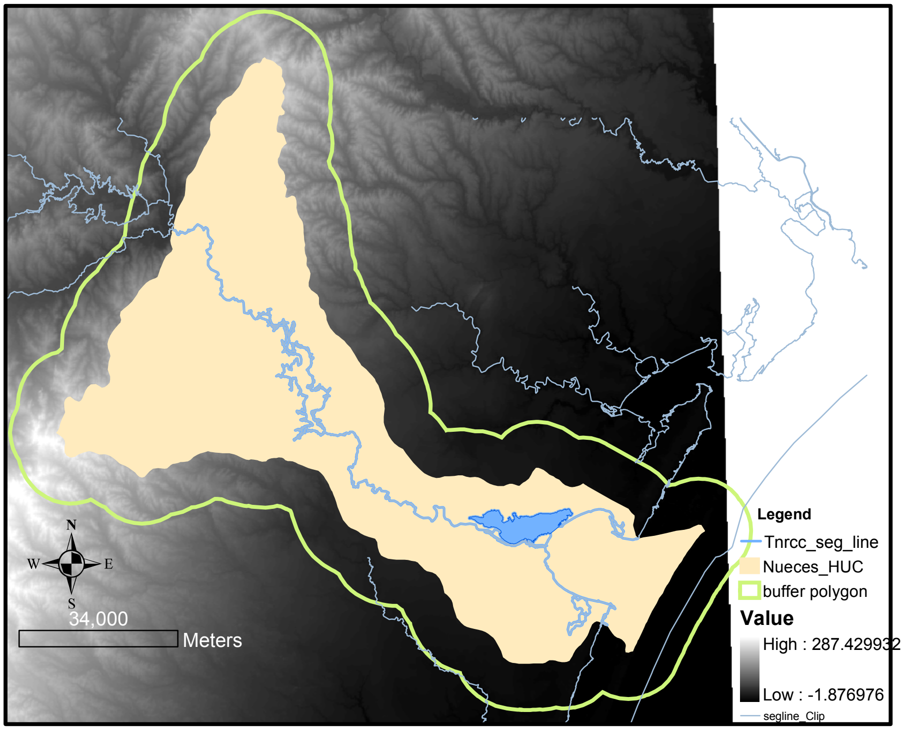


Figure 3.15 DEM, HUC area outline and buffer around Nueces Bay

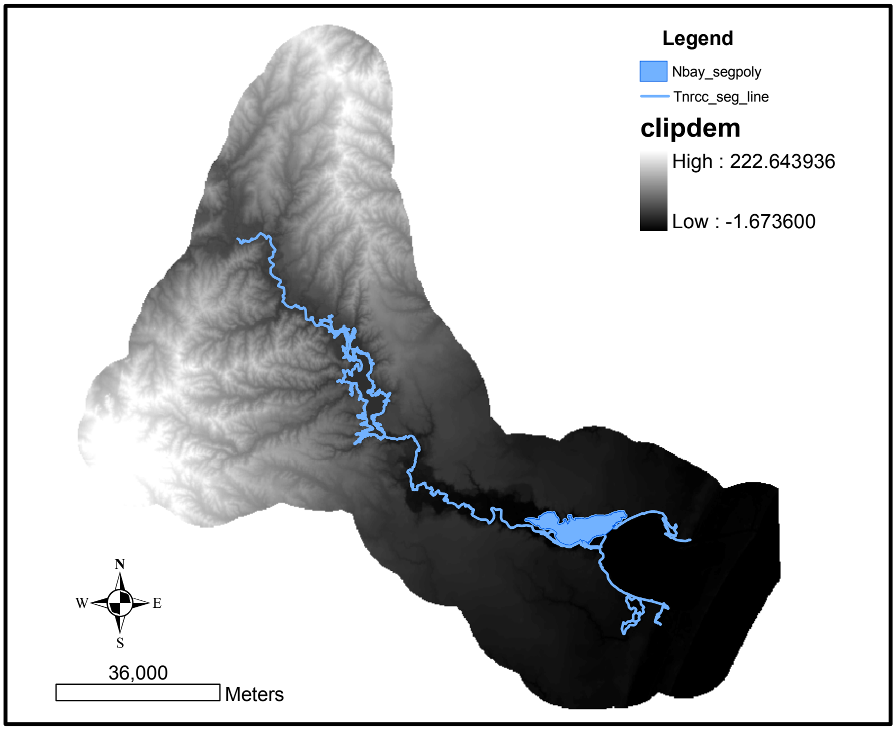


Figure 3.16 DEM buffer around Nueces Bay

The Digital Elevation models contain negative elevation values, up to a magnitude of 1.67m, as a result of the interpolation process from contour maps. These negative values are corrected using the "conditioning" command in ArcInfo Workstation in which any cell with a negative value is replaced with zero and all positive cells retain their original value. The resulting conditioned DEM is named *demcon*:

Grid: demcon = con (clipdem > 0, clipdem, 0)

3.2.5 Precipitation data

The precipitation data are obtained from the USDA-Natural Resources Conservation Service web link:

http://www.ftw.nrcs.usda.gov/prism/prismdata_state.html

These data were produced using the PRISM modeling system of the Spatial Climate Analysis Service at Oregon State University. PRISM (Parameter-elevation Regressions on Independent Slopes Model) is a hybrid statistical-geographic approach to mapping climate. It uses point measurements of climate data and a digital elevation model to generate estimates of annual, monthly and event-based climatic elements. For More information about PRISM, see the website of the Spatial Climate Analysis Service at Oregon State University:

http://www.ocs.orst.edu/prism/prism_new.html

Average Annual Precipitation for the state of Texas was downloaded as an interchange file (e.00). The file is then imported to a coverage using "import to coverage from interchange file" command in ArcToolbox. The precipitation coverage originally in geographic coordinate system is projected to Texas Centric Mapping System. The precipitation map for Texas is shown in Figure 3.17.

Using the HUC buffer layer created earlier, a geographic subset of the precipitation data is created using the "Clip" function in ArcMap. The resulting precipitation buffer *rain_nueces* is created as a shapefile and is shown in Figure 3.18.

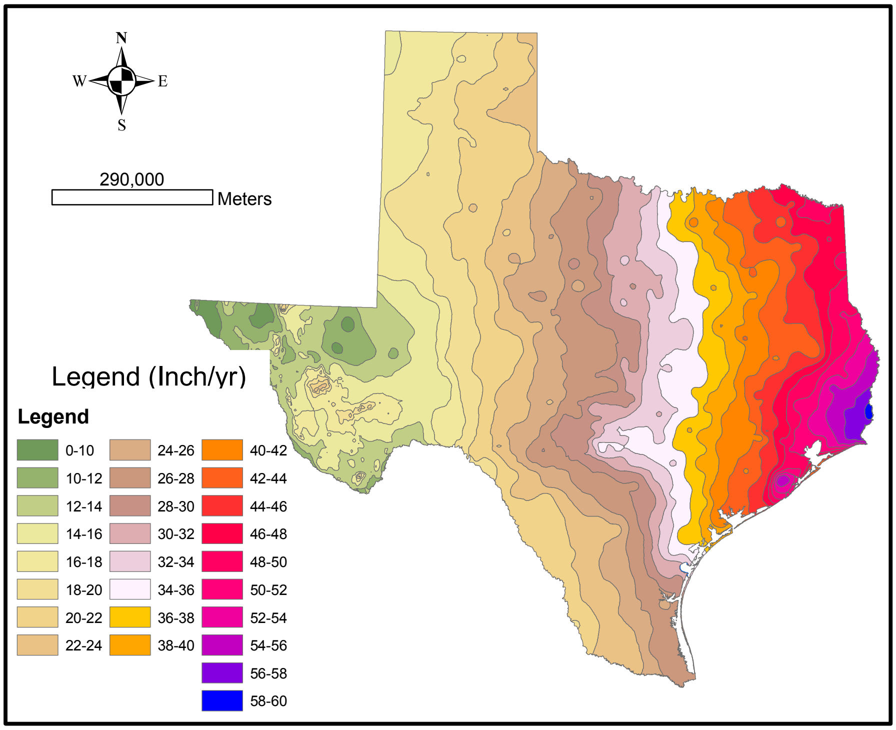


Figure 3.17 Annual precipitation (inches per year) coverage of Texas

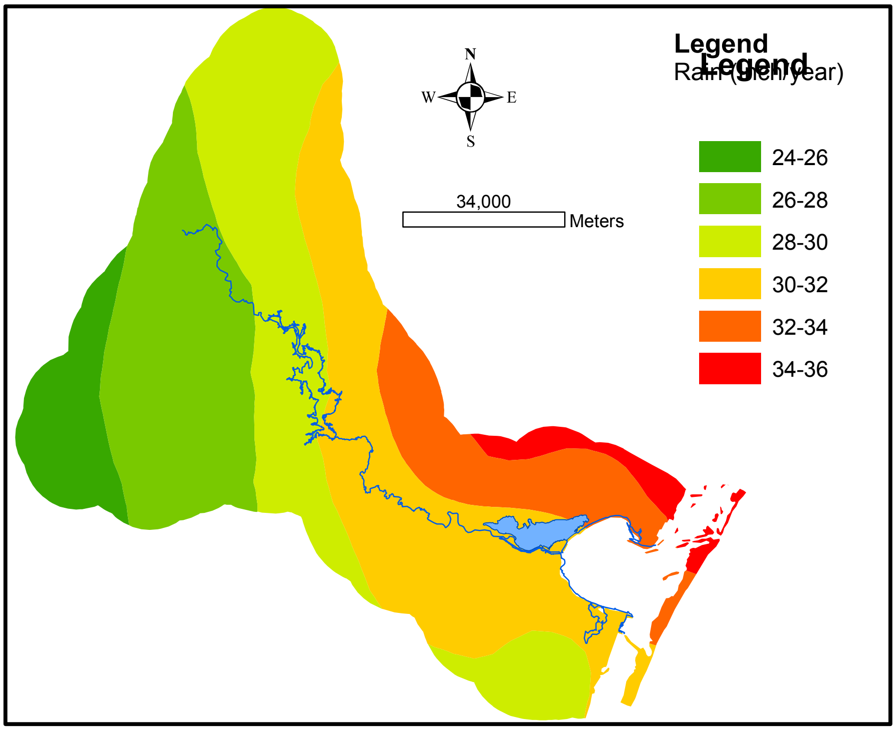


Figure 3.18 Precipitation buffer for the study area

3.2.6 Land cover/land use data

The National Land Cover Data (NLCD) is derived from the early to mid-1990s Landsat Thematic Mapper satellite data. The spatial resolution of the data is 30 meters and it is mapped in the Albers Conic Equal Area projection, NAD 83.

The NLCD for each state is offered as an 8 bit flat binary file (*. bin.gz) or as a Geo-TIFF (*. tif.gz) from USGS ftp site: http://edcftp.cr.usgs.gov/pub/data/landcover/states/

The Land cover data is also available for delivery via web downloads or CD media from the Seamless Data Distribution System: http://seamless.usgs.gov/.

After specifying the geographic extent of the study area from the Seamless Data Distribution System, the Land cover data was directly downloaded in a grid format and projected to Texas Centric Mapping System (Figure 3.19).

The National Land Cover Data (NLCD) is a 21-class land cover classification scheme applied consistently over the United States. The classification system used for NLCD is a revision of the Anderson land-use and land-cover classification system. For a more detailed discussion of the mapping and classification procedures of the NLCD data, go to: http://landcover.usgs.gov/natllandcover.html. The classification key of the National Land Cover Data is given in Table 3.9.

Category	Grid code	Class
Water	11	Open Water
	12	Perennial Ice/Snow
Developed Areas	21	Low Intensity Residential
	22	High Intensity Residential
	23	Commercial/Industrial/Transportation
Barren	31	Bare Rock/Sand/Clay
	32	Quarries/Strip Mines/Gravel Pits
	33	Transitional
Forested Upland	41	Deciduous Forest
	42	Evergreen Forest
	43	Mixed Forest
Shrubland.	51	Shrubland
Non-Natural Woody	61	Orchards/Vineyards/Other
Herbaceous Upland	71	Grasslands/Herbaceous
Planted/Cultivated	81	Pasture/Hay
	82	Row Crops
	83	Small Grains
	84	Fallow
	85	Urban/Recreational Grasses
Wetlands	91	Woody Wetlands
	92	Emergent Herbaceous Wetlands

Table 3.9 Classification key of the National Land Cover Data set

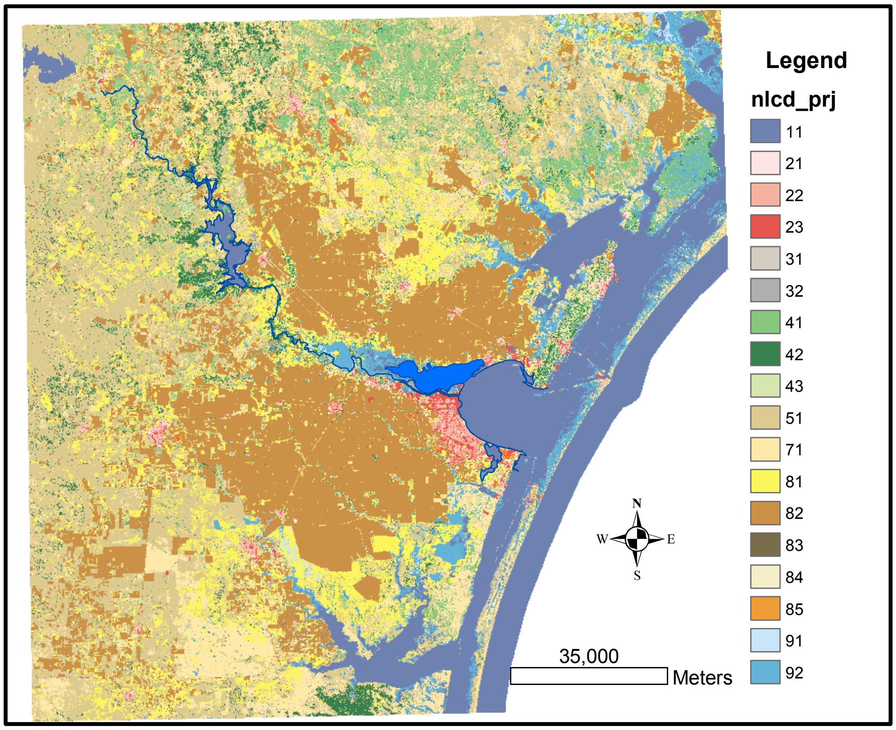


Figure 3.19 Land cover map downloaded from the Seamless Data Distribution

3.3 EVENT MEAN CONCENTRATIONS

Event Mean Concentration (EMC) is a method for characterizing pollutant concentrations in water from a runoff event. The value is determined by collecting (at a frequency proportional to the runoff or flow rate) a set of samples, taken at various points in time during a runoff event, into a single sample for analysis. The constituent concentration of the flow-averaged sample represents an Event Mean

Concentration. Event Mean Concentrations are used for this study as expected mean concentrations to calculate the land surface loads.

The EMC values of zinc are obtained from a previous study done for the CBBEP: "Characterization of Non-point Sources and Loadings to the Corpus Christi Bay National Estuary Program" (Baird et al, 1996). The investigators of this study compiled a database of Event Mean Concentration values for various non-point source constituents and different land use categories. The database was compiled using data applicable to the CCBNEP study area, including data from NPDES studies for Corpus Christi and the Galveston Bay National Estuary Program. When local data were not available for certain combinations of constituents and land uses, data from other areas were used (Baird et al, 1996). The Corpus Christi NPDES data base comprises samples collected at five urban stations that monitor runoff from areas consisting primarily of a single land use. For each of the five stations, samples were collected for six storm events during the period November 1992 through April 1993. For runoff EMCs the median value was considered a more appropriate measure of the central tendency of the concentration than the mean (Baird et al, 1996).Additional information about the methodology of EMC determination is found in the report by Baird et al (1996). EMC values for 18 constituents were obtained in this study, and are shown in Table 3.10.

Constituent	Land Use						
	Residential	Commercial	Industrial	Transportation	Cropland	Rangeland	Undev/Open
Total Nitrogen (mg/L)	1.82	1.34	1.26	1.86	4.40	0.70	1.50
Total Kjeldahl Nitrogen (mg/L)	1.50	1.10	0.99	1.50	1.7	0.20	0.96
Nitrate + Nitrite (mg/L as N)	0.23	0.26	0.30	0.56	1.6	0.40	0.54
Total Phosphorus (mg/L)	0.57	0.32	0.28	0.22	1.3	<0.01	0.12
Dissolved Phosphorus (mg/L)	0.48	0.11	0.22	0.10	--	--	0.03
Suspended Solids (mg/L)	41.0	55.5	60.5	73.5	107	1.0	70
Dissolved Solids (mg/L)	134	185	116	194	1225	245.0	--
Total Lead (m g/L)	9.0	13.0	15.0	11.0	1.5	5.0	1.52
Total Copper (m g/L)	15.0	14.5	15.0	11.0	1.5	<10	--
Total Zinc (m g/L)	80	180	245	60	16	6.0	--
Total Cadmium (m g/L)	0.75	0.96	2.0	< 1	1.0	<1.0	--
Total Chromium (m g/L)	2.1	10.0	7.0	3.0	<10.0	7.5	--
Total Nickel (m g/L)	< 10	11.8	8.3	4.0	--	--	--
BOD (mg/L)	25.5	23.0	14.0	6.4	4.0	0.5	--
COD (mg/L)	49.5	116	45.5	59	--	--	40
Oil and Grease (mg/L)	1.7	9.0	3.0	0.4	--	--	--
Fecal Coliform (colonies/100 ml)	20,000	6,900	9,700	53,000	--	37	--
Fecal Strep. (colonies/100 ml)	56,000	18,000	6,100	26,000	--	--	--

Table 3.10 EMC values by Constituent and Land Use Category for the CCBNEP Study Area (Baird et al, 1996)

Chapter 4: Methodology

The methodology presented in this chapter results in the development of a total zinc-loading model for Nueces Bay. First, a GIS based model is used to delineate the drainage area to the bay, in order to support calculations of the watershed-loading component of non-point sources. Next, an inventory of all sources of zinc, including point and non-point sources is established, along with an estimation of the flows and total zinc loads associated with them. Non-point sources of zinc to the Nueces Bay include land surface runoff, and atmospheric deposition. Point sources include municipal and industrial wastewater dischargers, and Lake Corpus Christi input through Nueces River. The final step was to incorporate all these mass loadings of zinc into a Continuously Stirred Tank Reactor (CSTR) model, and simulate total zinc concentrations in the Bay. The objective of this procedure is to be able to distinguish between contributions from controllable versus uncontrollable pollution sources, to ultimately define an action plan to tackle the biggest controllable pollution sources and improve water quality in the bay.

4.1 WATERSHED DELINEATION

Digital Elevation Models are needed in the delineation process since gravity drives flow over land surface. A procedure is developed to delineate the watershed for the water quality management Segment 2480 representing Nueces Bay. The procedure includes processing digital elevation models and using GIS tools to produce realistic watershed boundaries.

The objective of this task is to modify the traditional method of delineating watersheds, to consider the complications of the coastal drainage areas. Rather than delineating watersheds to points on a river networks, the delineation process was adjusted for coastal and low-lying regions with little slope, by defining areas draining to a length of river or a waterbody.

4.1.1 Processing the DEM

In this method of processing the Digital Elevation Models (DEM), the step of "burning in" the stream network to the DEM is disregarded. This process basically consists of overlaying the stream network to the digital elevation grid, and wherever the stream network coincides with a grid cell, that elevation is frozen, whereas any grid cell not coincident with the stream network, is raised by a fixed value (Samuels, 2001).

This alteration of the DEM is usually accompanied by distortion of the flow path and errors in flat areas, especially when the hydrography network is too intricate for the digital elevation model (Samuels, 2001). In the case of Nueces Bay project, the stream network used to delineate the watershed consists of the TCEQ stream segments, which, unlike the National Hydrography Dataset (NHD) network, only include the main drainage river network, and exclude small tributaries, artificial paths, and canals and ditches. Therefore, the step of burning the DEM was skipped in this process to keep the natural drainage path and avoid any discrepancies that may occur in DEM burning.

4.1.1.1 Filling sinks

The first step in processing the DEM for watershed delineation is filling sinks. DEM grids may contain artificial pits in the terrain due to errors in elevation or grid development. A pit or sink is where a set of one or more cells is surrounded on all sides by cells of higher elevation. In order to accurately delineate watersheds, artificial sinks are removed through the use of the Fill function in Arc Hydro tools within ArcGIS. This function alters the elevations of the sinking cells by using an interpolation function that ensures that the derived drainage paths are continuous, as shown in Figure 4.1 below. The Fill function in ArcHydro tools is run for the conditioned DEM *demcon* obtained earlier in section 3.24. The resulting filled DEM is *filled_dem*.

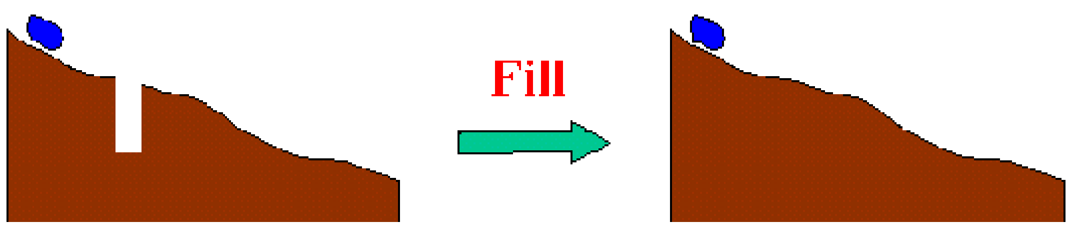


Figure 4.1 Filling an artificial pit in the DEM (Maidment, 2002)

4.1.1.2 Flow Direction

The flow direction function creates a grid in which each cell has a conventional value indicating the direction from that same cell to its steepest downslope neighbor cell. The numbering scheme used for computing flow direction is set by convention and is called the Eight Direction Pour Point

Method. In a DEM grid structure, there exist at most 8 cells adjacent to each individual grid cell. Water in a grid cell may flow only along one of the eight paths depicted by arrows in Figure 4.2

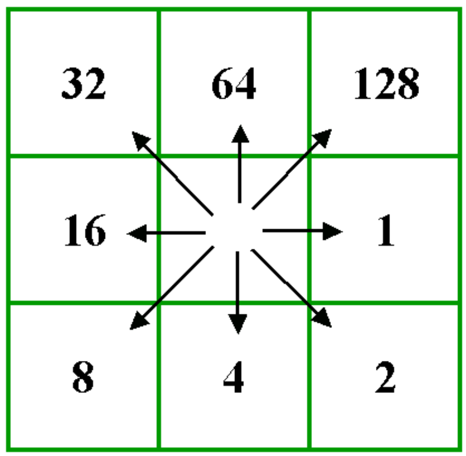


Figure 4.2 Eight-Direction Pour Point Model for Grid Operations

The 8- Direction Pour Point Model is based on flow in the direction of steepest decent from cell to cell. In other words, water will flow in the direction in which the greatest elevation decrease per unit distance is obtained. Each cell in the flow direction grid contains a value indicating the direction in which water will leave that cell. For example, water entering a flow direction cell with a value of 1 will leave that cell to the east. The flow direction grid is obtained by running the Flow Direction function in Arc Hydro tools within ArcMap for the filled DEM *filled_dem* obtained in section 4.1.1.1. Figure 4.3 shows the resulting flow direction grid, named *fdr_rawdem.*

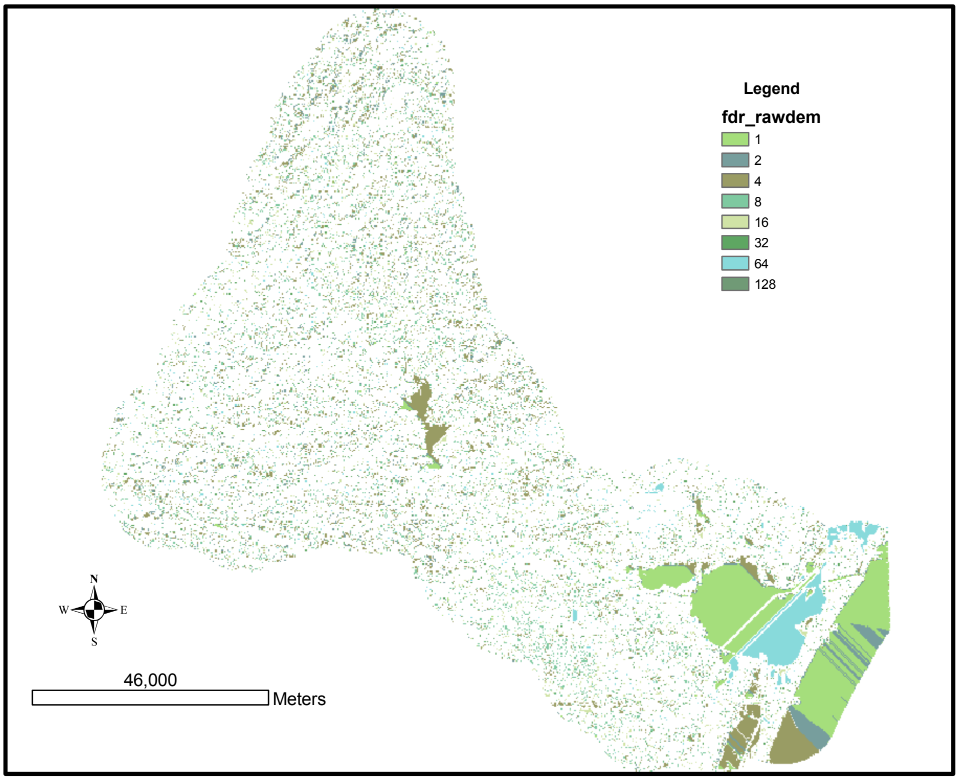


Figure 4.3 Flow direction grid for buffer area around Nueces Bay

For guidance on how to use the Fill and Flow direction functions of ArcHydro tools, see Exercise 5 " DEM's, Watershed and Stream Network Delineation" by Dr. Maidment in the link below: http://www.ce.utexas.edu/prof/MAIDMENT/giswr2002/giswr2002.htm

4.1.2 Delineating the watershed

4.1.2.1 TWISS tool

The Texas Integrated Water Simulation System (TWISS) is a custom Hydrologic Information System toolkit, initially created for the linkage of geospatial and temporal data to the Water Rights Analysis Package (WRAP). The toolkit was developed by Tim Whiteaker, from The Center for Research in Water Resources (CRWR). TIWSS uses the ArcGIS Hydro data model (Arc Hydro) as the data framework. Arc Hydro provides the tools and structure necessary to prepare data so that simulation models can easily extract required inputs from a geodatabase.

TIWSS utilizes a few important concepts to generate accurate results in an efficient manner. Two of these concepts are the delineation of watersheds from any feature class, and the use of watersheds as the basic processing unit for the accumulation of attributes (vs. using raster data).

Traditionally, watersheds are delineated in a GIS from a set of input points and a flow direction grid. The GIS uses the flow direction grid to determine which cells flow to a given input point before any other input point. That set of cells is merged to produce a watershed feature for the given input point. Thus, each point defines an outlet in the resulting watershed feature class.

The weakness of this approach occurs when the point is not placed in the proper location over the flow direction grid. If the point is not over a cell within a natural channel in the digital elevation model (or where a stream has been burned in), then a much smaller watershed will be delineated for that point than expected.

A more secure approach is to delineate watersheds to line or polygon features. As the watershed outlets, there is a much greater chance that the lines or polygon geometries will intersect a cell in the channel of the DEM.

TIWSS gives the user the capability of choosing which feature class to use as the Watershed outlets. This feature class is called the source layer. The source layer may contain point, line, or polygon features. This approach becomes particularly useful in flat areas, where the flow direction is more ambiguous.

ArcMap is the mapping and analysis component of the ArcGIS system. The TIWSS toolkit operates inside the ArcMap environment. The toolkit consists of an ArcMap toolbar with several buttons and commands (Figure 4.4).

Figure 4.4 TIWSS Toolbar

Additional Information about TWISS concept, parameters, and processing method can be found in the link: http://civilu.ce.utexas.edu/stu/mrinii/tiwss.htm

4.1.2.2 Delineating Watershed Using Twiss

The watershed delineation process is performed for the waterbody representing Nueces Bay (Segment 2482) using Twiss tool. The boundary of the watebody Segment 2482 is comprised of two line segments, which means that the watershed delineated to the polygon feature of Nueces Bay is the same as the one delineated to both boundary line segments. First, a geodatabase is created in ArcCatalog within ArcGIS software package. This geodatabase is named *wsh_delineation*. Second, a new feature dataset, named *delineation,* is created inside the geodatabase and projected to TCMS. The TCEQ segments (*Tnrcc_seg_line* and *Tnrcc_seg_poly*) are then imported as feature classes to the feature dataset.

A geodatabase is comprised of stand-alone tables, feature datasets, feature classes, and relationships in the ArcGIS environment. Standalone tables store non-spatial information, such as streamflow measurements. Feature classes store spatial information of the same type with the same attributes, such as rivers or bridges. Feature datasets organize feature classes into logical groupings, such as cartographic features (political boundaries, gage locations) and network features (rivers, confluences). Relationships connect features through common key attributes.

The feature dataset *delineation* and the flow direction grid fdr_rawdem are next opened in ArcMap, and the Twiss tool is installed by adding the corresponding dll file to the toolbar menu. The selection tool in ArcMap is then used to select the Nueces Bay segment from the TCEQ segments feature class Tnrcc_seg_poly. The selected segment 2482 will be the only polygon to which a drainage watershed will be determined.

Options for processing are set by clicking the 'Settings' button in Twiss toolbar. This opens the settings form. This form manages most of the inputs required for any operations in the Twiss toolkit.

The first input data required by TWISS is the flow direction grid. *Fdr_rawdem* is entered in the “Flow Direction Raster” drop down menu as shown in Figure 4.5.

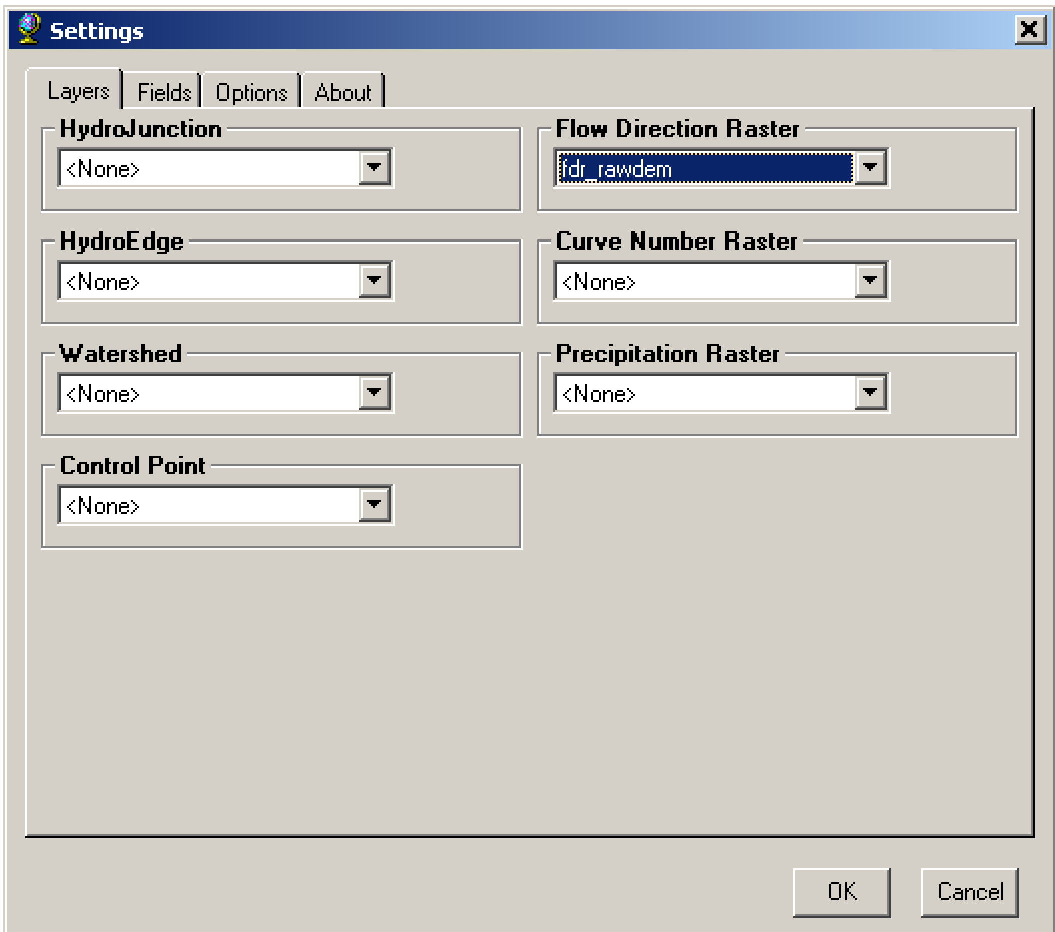


Figure 4.5 Layers input settings in Twiss tool

Next, the *Tnrcc_seg_poly feature class* is entered as the source layer in the Options menu, and the box “ Use selected features in source layer “ is also checked to permit the delineation for the selected segment only. Figure 4.6 shows the layout of the setting options.

During processing, TWISS also calculate the drainage area of the watershed delineated, so the drainage area units were set in sq meters.

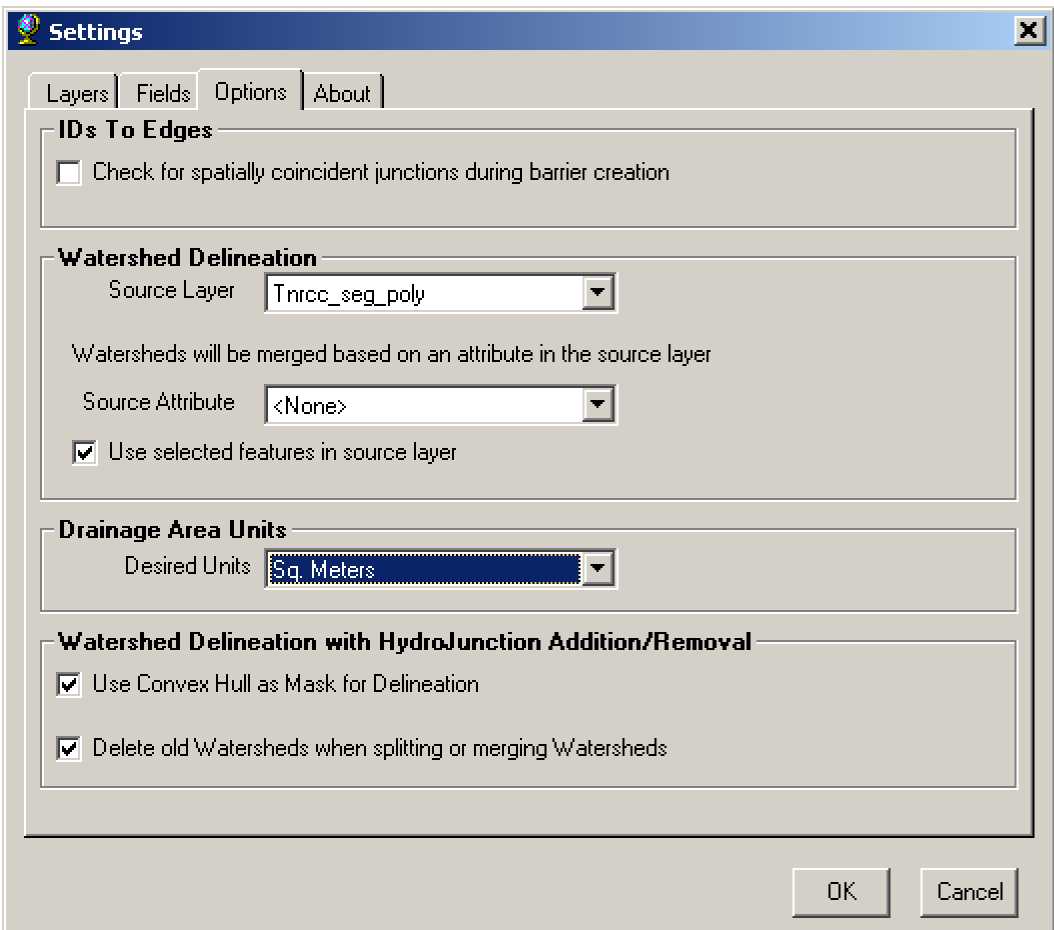


Figure 4.6 Options menu of TWISS toolkit

The final step is to run the delineation process. This is done by clicking on *Advance tools* in Twiss toolbar, and then *Delineate Watersheds* (Figure 4.7).

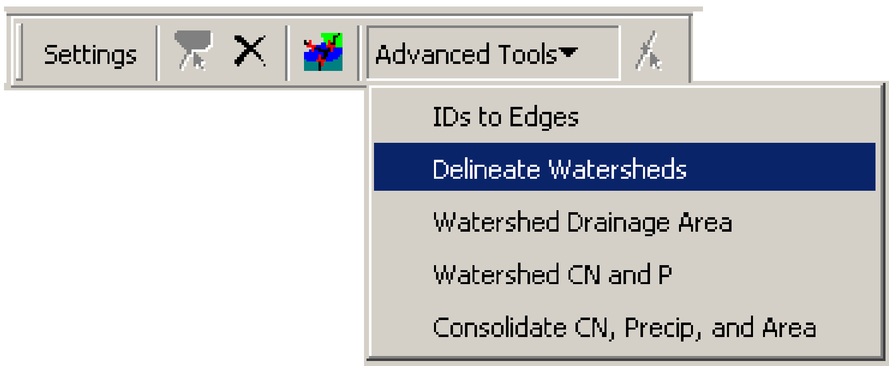


Figure 4.7 Process menu for watershed delineation

TWISS allows storing the output watershed either as a feature class inside a geodatabase or as a shapefile. The resulting watershed, named *Watershed_Nueces* is obtained after 5 to 10 minutes of processing, and includes the area of Nueces Bay (Figure 4.8). The drainage area of the watershed is around 935.5 Km^2.

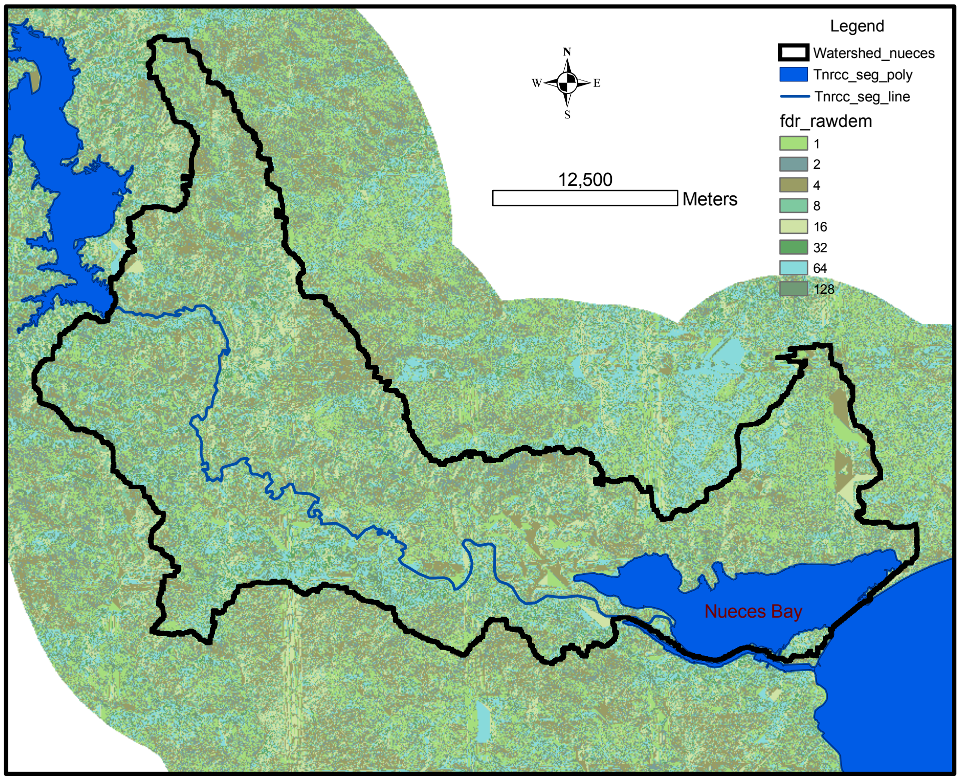


Figure 4.8 Watershed delineated for Nueces Bay

4.2 NON-POINT SOURCE LOADINGS OF ZINC

Non-point source pollution (NPS) refers to pollutants that come from a wide range of sources, which are usually diffuse and hard to define. These pollutants include substances found in agricultural and urban runoff. Examples of sources are animal wastes, construction activities, fertilizer, and pesticide application.

Non-point source pollution is generated during storm water runoff events. Runoff erodes or transports pollutants from wide, diffuse areas and delivers them to receiving waters. Atmospheric deposition can also be considered as non-point source pollution. The two major non-point sources of zinc to Nueces Bay are land surface runoff and atmospheric deposition. Loadings associated with both of these sources are discussed in this section.

4.2.1 Land surface load estimation

As water flows, it picks up and carries contaminants through streams and drainage areas of the ground depositing them into lakes, rivers, wetlands, and coastal waters. Runoff is a natural hydrologic phenomenon that is strongly influenced by land use and land cover.

A GIS method, similar to what has been done by Quenzer et al (1998), is presented for estimating the total loadings of zinc and runoff from land surface within the watershed delineated to Nueces Bay. The method is based on the capabilities of GIS tools to assess watershed characteristics, and perform calculations on geospatial data.

In this approach, watershed loadings of zinc to Nueces Bay represent the contribution of the constituent from runoff through each land cover category within the draining watershed. The watershed in question refers to the one previously delineated in section 4.1 and named *Watershed_Nueces.*

The GIS method for estimating non-point source loads of zinc from watershed runoff uses vector calculations within ArcGIS environment. The tasks undertaken are summarized in the following steps: 1) Reduce land cover data to the extent of the delineated watershed (*Watershed_Nueces)* and obtain a polygon coverage of land cover information, 2) Add mean annual precipitation information to the attribute table of the land cover vector data, 3) Use annual precipitation data to generate a runoff or flow data using a mathematical relationship between rainfall and runoff based on land use/land cover characteristics, 3) link each category of land-cover to Expected Mean Concentration of zinc and add these values to the attribute table of the land cover vector coverage , and 4) The land surface loads for each land cover drainage area are then calculated by multiplying the concentrations (EMC) values by the runoff. The sum of calculated runoff and zinc loads values in each land cover category represent the total flow and zinc loading respectively, attributed to non-point watershed pollution.

4.2.1.1 Average precipitation within land cover areas of Nueces watershed

The land cover grid *nlcd_prj* obtained in section 3.2.6 of chapter 3, needs to be clipped to the extent of the watershed area. This task is done by first converting the watershed shapefile to a grid or raster named *wsh-raster*, and then generating from it a mask called *mask30*, which is a grid with the same extent and cell size (30 m) as *wsh_raster* but with all its cell values equal to 1. This mask is obtained by dividing *wsh_raster* by itself in the ArcInfo environment. The final step of this clipping process is to generate the clipped land cover area *nlcd_nueces* in a grid format (Figure 4.9). This was done, by multiplying the larger area nlcd*_prj* by the smaller area of *mask30*.

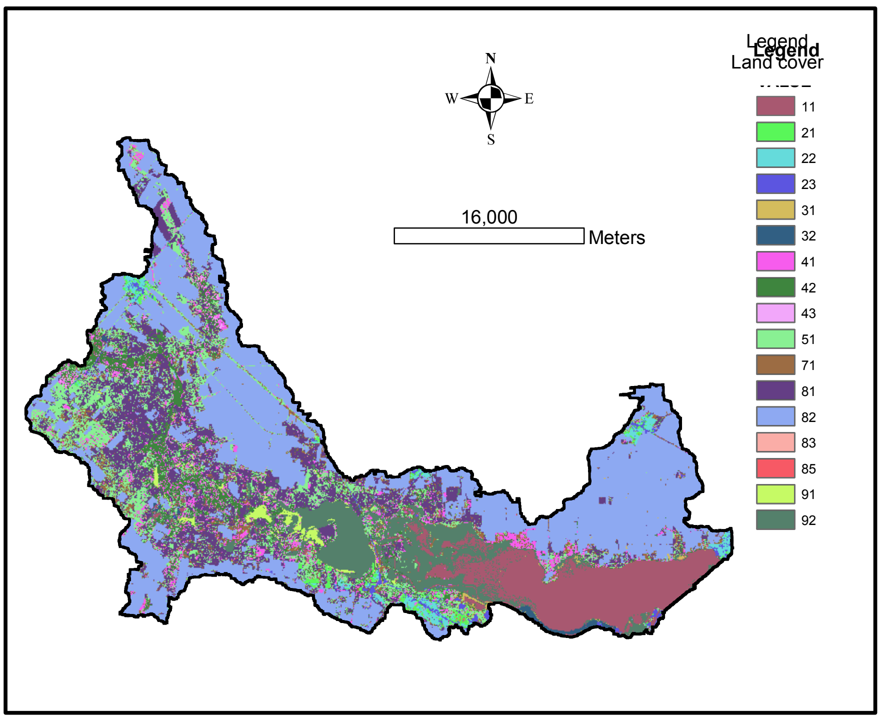


Figure 4.9 Clipped land cover grid *nlcd_nueces*

All the steps involved in clipping the land cover grid to the watershed area are carried out in ArcInfo Workstation using the following commands:

Grid : setcell wsh_raster

Grid : setwindow wsh_raster wsh_raster

Grid : mask30=wsh_raster/wsh_raster

Grid : nlcd_nueces = mask30*nlcd_prj

The next step is to convert the land cover grid *nlcd_nueces* to a polygon coverage format as *nlcd_cov*. The command in ArcToolbox "import grid to polygon coverage" is used to perform this conversion, which adds information on surface area [*Area*] and perimeter [Perimeter] of each polygon to the attribute table of the land cover vector.

The precipitation buffer shapefile obtained in section 3.2.5 of chapter 3 is converted to a coverage, then to a grid *rain_grid* using ArcToolbox. *nlcd_cov* is then imported to a geodatabase as a feature class, and both data files *rain_grid* and *nlcd_cov* are added in ArcMap (Figure 4.10). To obtain average annual precipitation for each land cover polygon, the zonal statistics function included in the spatial analyst tool is used in ArcMap.

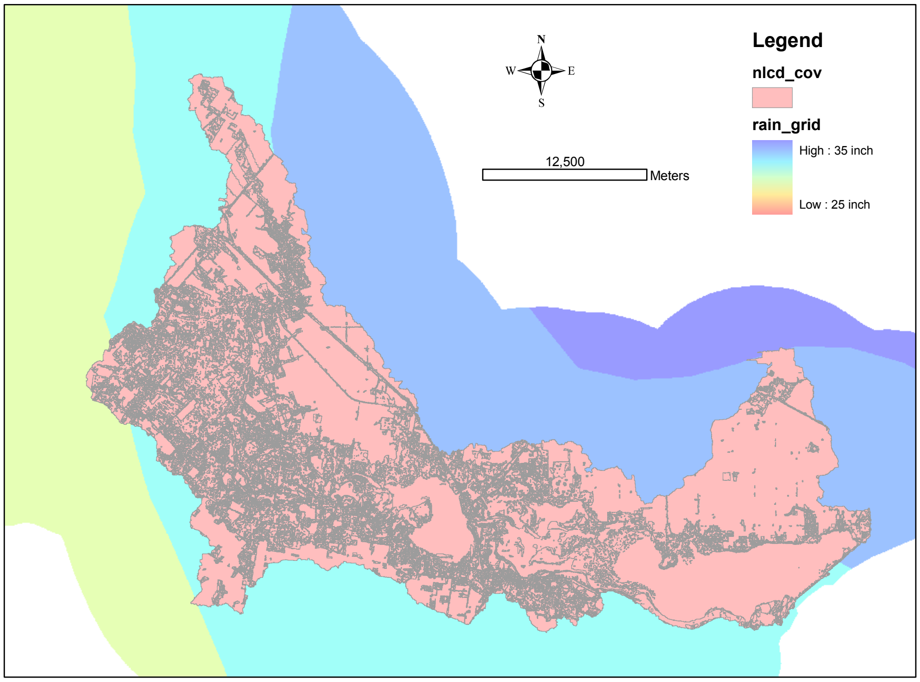


Figure 4.10 Watershed Land cover coverage and annual mean precipitation buffer grid in the study area

The Zonal Statistics is a Spatial Analyst function that computes statistics for each zone of a zone dataset based on the information in a value raster (ESRI, 2001). The spatial analyst extension is added in ArcMap, and zonal statistic is opened from the Spatial Analyst dropdown menu (Figure 4.11).

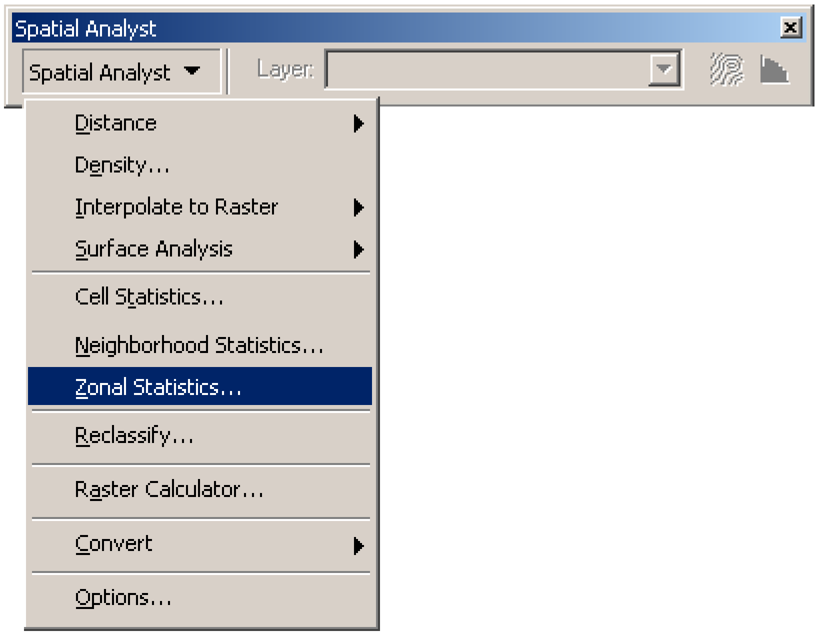


Figure 4.11 Zonal statistic function in spatial analyst toolbar

As shown in figure 4.12, the zone dataset is the land cover layer *land_cov*. Land_cov_ID is a unique identifier of each polygon zone in the land cover attribute table, and is used as the zone field. The input raster is *rain_grid*, which contains the annual precipitation input values used in calculating the output for each zone. The output table is the resulting zonal statistics table that can be joined to the land cover zone layer to display a statistic per zone. Operations that are completed by Zonal Statistics return the mean, sum, minimum, maximum, or range of values from the precipitation dataset that fall within a specified zone of land cover dataset (Figure 4.13).

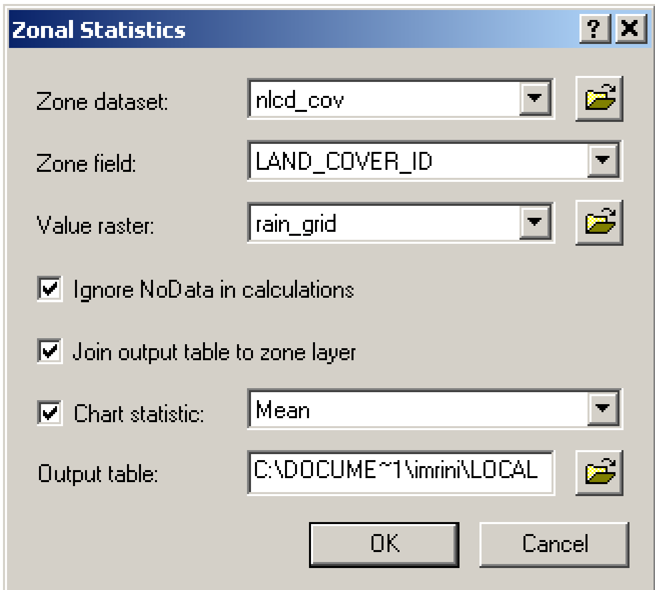


Figure 4.12 View of zonal statistics input box

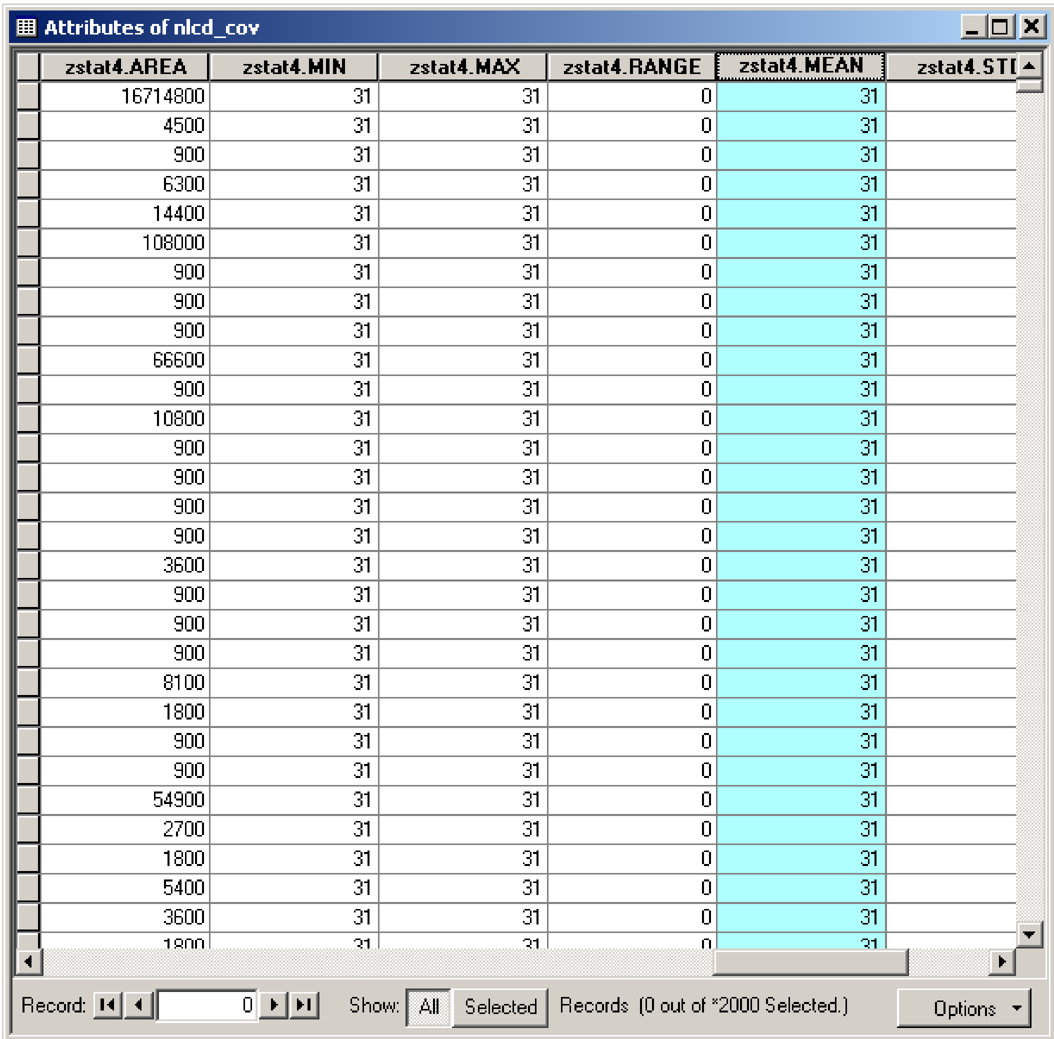
After running Zonal Statistics, an output table *zstat4* is created, and temporary joined to the land cover attribute table (Figure 4.14). To permanently store the mean annual precipitation values (in mm) within land cover zones, a new field *mean_preci* is added in the attribute table of *land_cov*, and a right click on that field is made to open the function *calculate values* and then the following equation is entered: [Mean_preci] = 25.4 * zstat4.mean.

Stats of "rain_grid" Within Zones of "nlcd_cov"

OID	VALUE	COUNT	AREA	MIN	MAX	RANGE	MEAN	STD	SUM
0	2	18572	16714800	31	31	0	31	0	575732
1	3	5	4500	31	31	0	31	0	155
2	4	1	900	31	31	0	31	0	31
3	5	7	6300	31	31	0	31	0	217
4	6	16	14400	31	31	0	31	0	496
5	7	120	108000	31	31	0	31	0	3720
6	8	1	900	31	31	0	31	0	31
7	9	1	900	31	31	0	31	0	31
8	10	1	900	31	31	0	31	0	31
9	11	74	66600	31	31	0	31	0	2294
10	12	1	900	31	31	0	31	0	31
11	13	12	10800	31	31	0	31	0	372
12	14	1	900	31	31	0	31	0	31
13	15	1	900	31	31	0	31	0	31
14	16	1	900	31	31	0	31	0	31
15	17	1	900	31	31	0	31	0	31
16	18	4	3600	31	31	0	31	0	124
17	19	1	900	31	31	0	31	0	31
18	20	1	900	31	31	0	31	0	31
19	21	1	900	31	31	0	31	0	31
20	22	9	8100	31	31	0	31	0	279
21	23	2	1800	31	31	0	31	0	62
22	24	1	900	31	31	0	31	0	31
23	25	1	900	31	31	0	31	0	31
24	26	61	54900	31	31	0	31	0	1891
25	27	3	2700	31	31	0	31	0	93
26	28	2	1800	31	31	0	31	0	62
27	29	6	5400	31	31	0	31	0	186
28	30	4	3600	31	31	0	31	0	124
29	31	2	1800	31	31	0	31	0	62
30	32	2	1800	31	31	0	31	0	62
31	33	7	6300	31	31	0	31	0	217
32	34	1	900	31	31	0	31	0	31
33	35	1	900	31	31	0	31	0	31
34	36	1	900	31	31	0	31	0	31
35	37	1	900	31	31	0	31	0	31
36	38	5	4500	31	31	0	31	0	155
37	39	2	1800	31	31	0	31	0	62

Record: 1 Show: All Selected Records (0 out of 55032 Selected.) Options

Figure 4.13 Statistics table and graph of mean precipitation values within zones of land cover area, created after running Zonal Statistics tool



Attributes of nlcd_cov

zstat4.AREA	zstat4.MIN	zstat4.MAX	zstat4.RANGE	zstat4.MEAN	zstat4.STI
16714800	31	31	0	31	
4500	31	31	0	31	
900	31	31	0	31	
6300	31	31	0	31	
14400	31	31	0	31	
108000	31	31	0	31	
900	31	31	0	31	
900	31	31	0	31	
900	31	31	0	31	
66600	31	31	0	31	
900	31	31	0	31	
10800	31	31	0	31	
900	31	31	0	31	
900	31	31	0	31	
900	31	31	0	31	
900	31	31	0	31	
3600	31	31	0	31	
900	31	31	0	31	
900	31	31	0	31	
900	31	31	0	31	
8100	31	31	0	31	
1800	31	31	0	31	
900	31	31	0	31	
900	31	31	0	31	
54900	31	31	0	31	
2700	31	31	0	31	
1800	31	31	0	31	
5400	31	31	0	31	
3600	31	31	0	31	
1800	31	31	0	31	

Record: 0 Show: All Selected Records (0 out of *2000 Selected.) Options

Figure 4.14 View of the temporary zonal statistic table joined to *nlcd_cov* attribute table

4.2.1.2 Precipitation-runoff relationship

The mathematical equations relating rainfall to runoff are taken from a previous study done by a former UT student (Ann Quenzer, 1998) in her thesis entitled "A GIS assessment of the Total Loads and water Quality in the Corpus Christi Bay System". The general method in this study uses a regression tool to determine the relationship stream flow, precipitation, and percent land use. The USGS streamflow gauges were obtained for the area draining to the Corpus Christi Bay system, and a weighted flow accumulation operation was used to determine the average rainfall for each drainage area and by determining the average runoff per unit area at each USGS gauge station, a mathematical equation is established between precipitation and runoff. Equations were calculated for four types of land use: agricultural, range, urban and areas representing water (wetlands, streams, estuaries, bays...).

The land cover categories used in this study are classified within the four land use types used in Quenzer's study (1998) to obtain applicable runoff equations. These equations are summarized in Table 4.1.

Land cover category	Classification	Runoff equation
11 Open Water 12 Perennial Ice/Snow	Water	Q = 0
21 Low Intensity Residential 22 High Intensity Residential 23 Commercial/Industrial/Transportation 85 Urban/Recreational Grasses	Urban	Q = 0.24 * P
81 Pasture/Hay 82 Row Crops 83 Small Grains 84 Fallow	Agriculture	Q = 0.008312 * exp (0.011415 * P)
31 Bare Rock/Sand/Clay 32 Quarries/Strip Mines/Gravel Pits 33 Transitional 51 Shrubland 71 Grasslands/Herbaceous 91 Woody Wetlands 92 Emergent Herbaceous Wetlands 41 Deciduous Forest 42 Evergreen Forest 43 Mixed Forest	Range land, Barren, Forest Land, other	Q = 0.0053 * exp (0.010993 * P)

Table 4.1 Runoff /precipitation relationship for land cover categories

4.2.1.3 Zinc Event Mean Concentration values

As discussed in subchapter 3.3, the zinc EMC values for some land use categories were obtained from a study done by Baird et al (1996). Table 4.2 shows these EMC values (µg/l).

Land use description	Zinc EMC (μg/l)
Residential	80
Commercial	180
Industrial	245
Transportation	60
Agriculture	16
Range	6
Mixed	141

Table 4.2 Zinc EMC values for land use classes (Baird et al, 1996)

To link zinc EMC values to land cover categories of the NLCD dataset, The EMC values obtained from Baird et al (1996) were adjusted to reflect land cover types instead of land use classes. Table 4.3 shows the corresponding EMC for each grid code of land cover. Grid codes 21 and 22 are assigned residential EMC value, while EMC value for grid code 23 is an average of commercial, industrial and transportation EMC values. Grid codes between 31 and 43 are given the EMC for rangeland use. Grid codes between 81 and 84 are considered to have agriculture EMC, and grid code 85 has an EMC equal to the average of residential and commercial EMC values.

Land cover grid code, description	Zinc EMC (µg/l)
21 Low Intensity Residential 22 High Intensity Residential	80
23 Commercial/Industrial/Transportation	162
31 Bare Rock/Sand/Clay 32 Quarries/Strip Mines/Gravel Pits 33 Transitional 51 Shrubland 71 Grasslands/Herbaceous 91 Woody Wetlands 92 Emergent Herbaceous Wetlands 41 Deciduous Forest 42 Evergreen Forest 43 Mixed Forest	6
81 Pasture/Hay 82 Row Crops 83 Small Grains 84 Fallow	16
85 Urban/Recreational Grasses	130

Table 4.3 Adjusted zinc EMC values for land cover categories

To add the EMC values to the land cover vector data, the attribute table of *land_cov* is opened in ArcMap, and a new field called EMC is added to the table. The edit mode is started, by clicking on “start editing” in the Editor dropdown menu bar, then a right click on the EMC field column to “calculate values” opens the field calculator. A simple VBA script code is written to assign EMC values for each land cover grid code. This code is given below:

```
If [GRID_CODE] = 11 or [GRID_CODE] = 12 then
      [EMC] = 0
elseif [GRID_CODE] = 21 or [GRID_CODE] = 22  then
      [EMC] = 80
elseif [GRID_CODE] = 31 or [GRID_CODE] = 32 or [GRID_CODE] = 33 or
[GRID_CODE] = 51 or [GRID_CODE] = 71 or [GRID_CODE] = 91 or
[GRID_CODE] = 92 or [GRID_CODE] = 41 or [GRID_CODE] = 42 or
[GRID_CODE] = 43 then
      [EMC] = 6
elseif [GRID_CODE] = 81 or [GRID_CODE] = 82 or [GRID_CODE] = 83 or
[GRID_CODE] = 84 or [GRID_CODE] = 61 then
      [EMC] = 16
elseif [GRID_CODE] = 85 then
      [EMC] = 130
elseif [GRID_CODE] = 23 then
      [EMC] = 162
End if
```

The field calculator is set on the advanced mode for pre-logic VBA script code, and the code above is pasted into it as shown in Figure 4.15. After running the field calculator process, EMC values for each land cover polygon are calculated and added in the EMC field column of the attribute table.

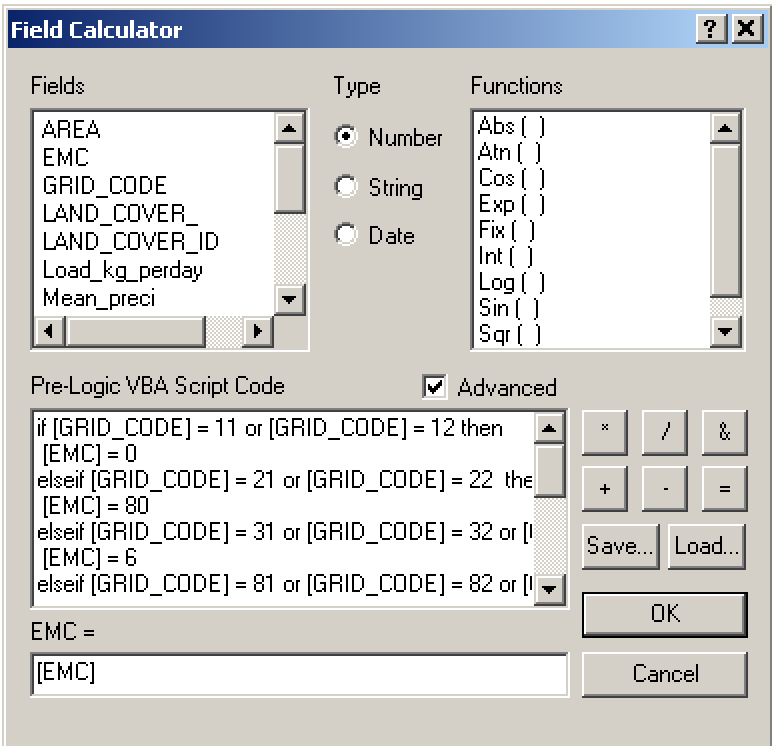


Figure 4.15 Field calculator for EMC values in ArcMap

4.2.1.4 Runoff and land surface loads of zinc

The runoff values (mm/yr) for each land cover zone are calculated using the equations given in 4.2.1.2. First the attribute table of *land_cov* is opened and a new field called *runoff* is created. After starting the edit mode, the field calculator is opened by right clicking on *runoff* column and selecting “calculate values”. The VBA script code for calculating runoff using rainfall-runoff equations is given below, and is entered into the field calculator (Figure 4.16).

```
If [GRID_CODE] = 11 or [GRID_CODE] = 12 then
       [Runoff] = 0
elseif [GRID_CODE] = 21 or [GRID_CODE] = 22 or [GRID_CODE] = 23
or [GRID_CODE] = 85 then
       [Runoff] = 0.24 * [Mean_preci]
elseif [GRID_CODE] = 31 or [GRID_CODE] = 32 or [GRID_CODE] = 33
or [GRID_CODE] = 51 or [GRID_CODE] = 71 or [GRID_CODE] = 91 or
[GRID_CODE] = 92 or [GRID_CODE] = 41 or [GRID_CODE] = 42 or
[GRID_CODE] = 43 then
       [Runoff] = 0.0053 * Exp (0.010993 * [Mean_preci])
elseif [GRID_CODE] = 81 or [GRID_CODE] = 82 or [GRID_CODE] = 83
or [GRID_CODE] = 84 then
       [Runoff] = 0.008312 * Exp (0.011415 * [Mean_preci])
End if
```

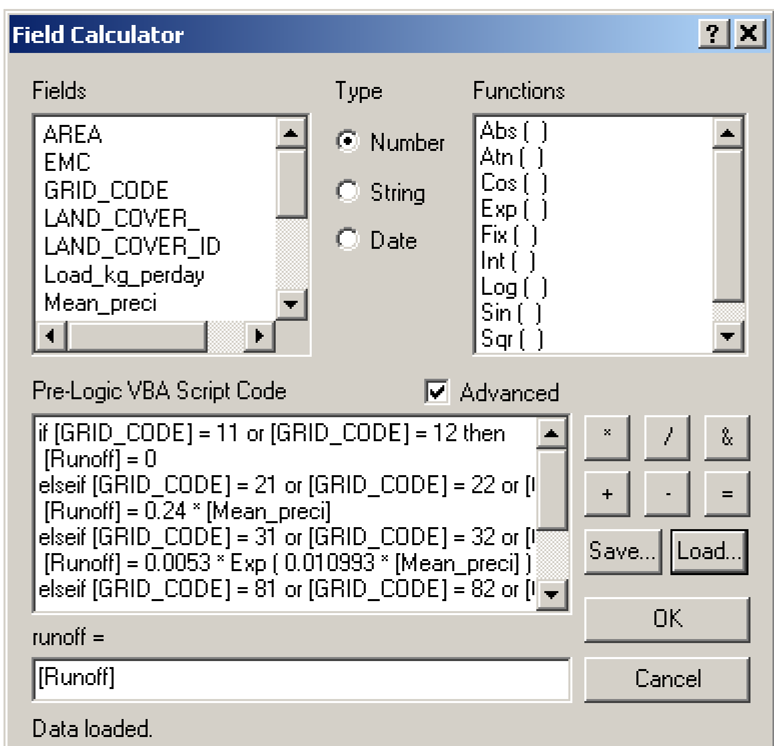


Figure 4.16 VBA code in field calculator for runoff (mm/yr)

The runoff values obtained after running the field calculator process are in mm per year. To obtain runoff in m^3/s, a new field called *Runoff_cms* is first created in the attribute table of *land_cov*. Values in *Runoff_cms* (m^3/s) are obtained, by multiplying values of *runoff* (mm/yr) by the polygon area [*Area*], and adjusting the units. The equation entered in the field calculator of *Runoff_cms* is as follow:

$$[Runoff\_cms] = \frac{[runoff]*[Area]}{1000*365*86400}$$

The land surface loads for each land cover drainage area are calculated by multiplying the concentrations (EMC) values by the runoff values. A new field *Load_kg_perday* representing the surface loads of zinc (kg / day) is created in the land cover attribute table. Next, the edit mode is started, and right clicking on the field column *Load_kg_perday* and selecting "calculate values" opens the field calculator. The following equation is entered in the field calculator (as shown in Figure 4.17):

$$[Load\_kg\_perday] = [Runoff\_cms]*[EMC]*86400*10^{-6}$$

After running the calculation process, the land surface loads of zinc from each land cover zone are calculated and added in the attribute table of *land_cov*, within the column *Load_kg_perday*.

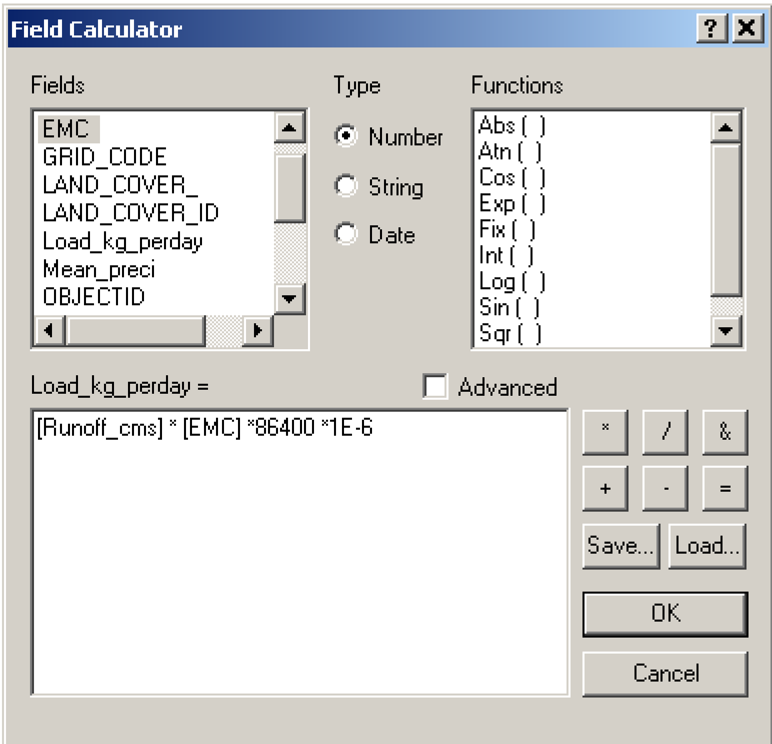


Figure 4.17 Field calculator of land surface loads of zinc

4.2.2 Atmospheric deposition

A significant source of accumulated pollutants in urban areas originates from atmospheric deposition. Atmospheric deposition can occur as dry deposition of airborne particles, or as wet deposition, which includes constituents carried by precipitation. For bays and estuaries that receive limited freshwater inflow, atmospheric sources can provide a significant portion of the total load of certain constituents.

Data on atmospheric deposition within Nueces Bay study area is taken from the results of the study *Atmospheric Deposition Monitoring within the*

Corpus Christi Bay National Estuary Program Study Area (Wade et al, 2000). This study involved recording of meteorological data and collection of samples of air and rain deposition from two sampling sites, for analyses on nutrients and trace elements. The first site, sampled between April 1997 and August 1999, is located at Texas A&M University-Corpus Christi (TAMUCC) campus on Ward Island. The second site, sampled between June 1997 and August 1999, is located at White Point on the north shore of Nueces Bay. Approximate locations of the two monitoring stations mentioned above are shown in Figure 4.18.

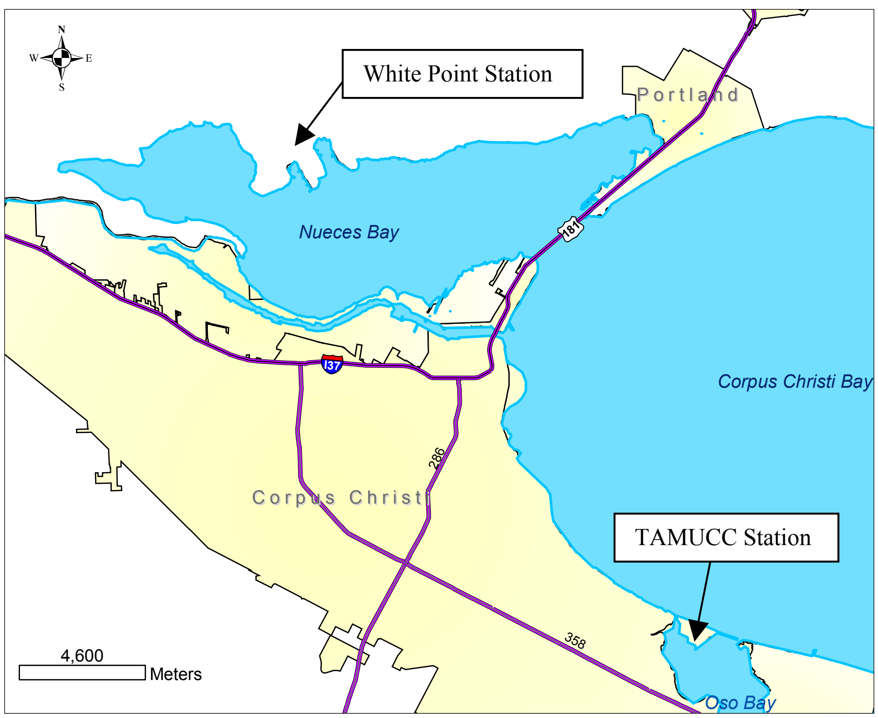


Figure 4.18 Location of atmospheric deposition monitoring stations

Among the sources of information contained in the study by Wade et al (2000) are the Corpus Christi Bay National Estuary Program, EPA environmental Monitoring and Assessment Program, and NOAA National Status and Trends Program. Winds in the region are predominately from the southeast (March-September), and north (November-February) (Wade et al, 2000).

The cumulative deposition of zinc at White Point was 1 kg/km^2-yr for wet deposition and 91 kg/km^2-yr for dry deposition, whereas the cumulative deposition of zinc at TAMUCC was 3 kg/km^2-yr for wet deposition, and 52 kg/km^2-yr for dry deposition (Wade et al, 2000). The total deposition (wet+ dry) was 55 kg/km^2-yr at TAMUCC, and 91 kg/km^2-yr at White Point. Atmospheric deposition almost doubles in White Point station compared to TAMUCC station, most likely because it includes air pollution coming from Corpus Christi industries. The best representative station for reflecting atmospheric deposition in Nueces Bay is the White Point station because of its close location to the bay.

4.3 Point Source Loading

4.3.1 Permitted dischargers

Information about permitted dischargers to Nueces Bay are based on data obtained from the Texas Commission on Environmental Quality (TCEQ), and data compiled in a previous study done by Armstrong and Ward (1997), entitled "Analysis of Point source discharges (including oil field brine discharges) in the Corpus Christi Bay National Estuary Program study area". This study aimed to characterize the current status and spatial and temporal trends in permitted point source loadings of constituents into the Corpus Christi system.

An inventory and description of the permitted point source dischargers to Nueces Bay, taken into account in this study are given below:

1. Central Power and Light Company (TDPES permit No. 01244): a steam electric generating facility located at 2002 Navigation Boulevard, one and a half miles west of the Corpus Christi Harbor Bridge in the city of Corpus Christi, Nueces County, Texas. The Nueces Bay Power station withdraws water from the Corpus Christi ship channel for once through cooling water which discharges to outfall 001. Other wastewaters routed to outfall 101, are generated from water purchase from the city of Corpus Christi and used for various units in the plant.

   The permit (active till April 1, 2005) authorizes the discharge of once through cooling water via outfall 001 at a daily average flow not to exceed 500 MGD, and the discharge of low volume, wastewater, metal cleaning waste, and storm water via outfall 101. Recent reported flow data are given in Table 4.4.

	Period from June 1998 to May 2000
Daily Average Flow (m^3/s)	17.35
Daily Maximum Flow (m^3/s)	21.45

Table 4.4 Report Flow data through OTFL 00, for the period June 1998 through May 2000

2. City of Portland (Permit No. 10478-001): is authorized to treat and dispose of wastes from the City of Portland Wastewater treatment facility (located at 1095 Moore Avenue, San Patricio County) to a drainage ditch, thence to the Nueces Bay. Permit active till April 1, 2005
3. Sublight Enterprises, Inc. (permit No. 11096-001): is authorized to treat and dispose of wastes from the Portland Inn Wastewater treatment facility (located approximately 200 feet north of U.S Highway 181) to Nueces Bay. Permit active till April 1, 2005.
4. Coastal Chemical Co., L.L.C (permit No. 03780) is authorized to treat an dispose of wastes from a bulk storage facility for distribution of organic chemicals (located on the west side of Floerke Road) to a series of roadsides ditches, thence though a culvert to an unnamed tributary of Nueces Bay. The permit expired on October 27, 2000.

Figure 4.19 displays a map view of approximate locations of the four permitted dischargers to Nueces Bay. According to the study by Armstrong et al (1997), the number of self-reporting requirements for metals from municipal and industrial point source dischargers were extremely small. All municipal dischargers did not report metals and some industrial dischargers were not required to report some constituents including zinc. Consequently, to obtain a reasonable estimate of constituents, the TPCs (typical pollutant concentrations) were used in this study to estimate loadings to segments of the Corpus Christi Bay complex study area. These TPC values represent an approximation of the pollutants concentrations in a discharge of a typical plant. They were drawn primarily from the EPA's *Development Documents for Effluent Limitations, Guidelines, and Standards*, and are based on monitoring studies conducted between mid-1970s and the mid-1980s at a representative sample of facilities engaged in the industrial activity (Armstrong et al, 1997). Those TPCs were multiplied by actual discharge flows calculated from self-reporting data to get loads for each dischargers (Armstrong et al, 1997). In the report by Armstrong et al (1997), caution was made on the accuracy of the TPCs and the load estimates made from them due to their tentative nature.

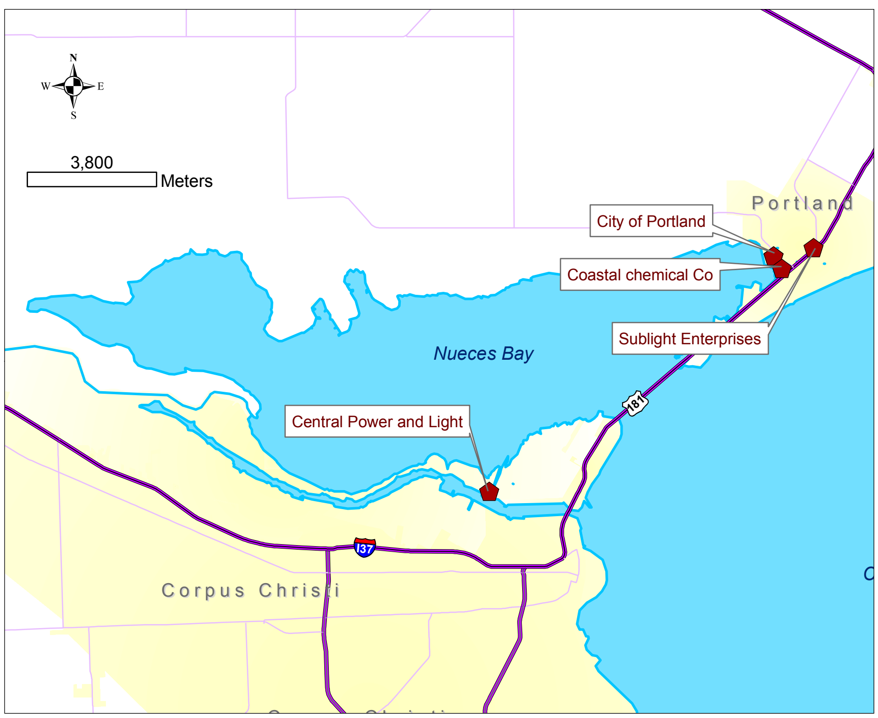


Figure 4.19 Locations of permitted dischargers to Nueces Bay

For Nueces Bay, or Segment 2482, results of the analysis done by Armstrong et al (1997) concluded that 12% of the industrial discharge of zinc is based on measured loads, and 100% of the municipal discharge is based on estimated loads. The flows and zinc loading values to Nueces Bay, obtained from this study for the year 1995 are summarized below:

Industrial flow = 15.64 m^3/s

Municipal flow = 0.05 m^3/s

Point source loadings of zinc = 0.71 kg/day

The industrial flow mainly consists of the CP&L station flow. Recent reporting flow data of CP&L facility indicate an average flow of 17.35m^3/s between June 1998 and May 2000 (Table 4.4). To have an accurate value of industrial flow, it is obtained by averaging the 1995 industrial flow value (15.64 obtained from the report (Armstrong &Ward, 1997) and the average CP&L flow (17.35 m^3/s) reported in the permit data, and reflecting the period between 1999 and 2000.Therefore:

Average industrial flow = Average CP&L flow = 16.5 m^3/s

Municipal return flows discharged to Nueces Bay are relatively small and consist primarily of wastewater discharges. The municipal flow (0.05 m^3/s) consists of reported flow data from the city of Portland and is assumed not to have significantly changed. The total flow from permitted dischargers is equal to the sum of industrial and municipal flow:

Total flow = Industrial (CP&L) flow + Municipal = 16.55 m^3/s

4.3.2 Lake Corpus Christi point source load

Lake Corpus Christi is considered as a point source pollutant contributor to Nueces Bay, through constituent transport into Nueces River. The mean flow leaving the lake at the Nueces River gauging station near Mathis, TX is around 17.36 m^3/s during 30 years of flow records (1971-2000). Only a portion of this flow discharges to Nueces Bay, due to withdrawals from the City of Corpus Christi. Inflow from the Nueces River provides most of the freshwater inflow to the Nueces estuary, and the station at Callalen accounts for all of the measured inflow to the estuarine system (USGS, 2001).

USGS Streamflow gauging station 08211500, Nueces River at Callalen (Figure 4.20), is located at the Callalen Dam, a small rock fill dam that serves as a barrier to saltwater intrusion from Nueces Bay. Streamflow in the Nueces River at Callalen is regulated by upstream reservoirs (USGS, 2001). The mean flow measured at the USGS 08211500, Nueces River at Callalen between 1991 and 2000 is 2.47 m^3/s (USGS, 2000).

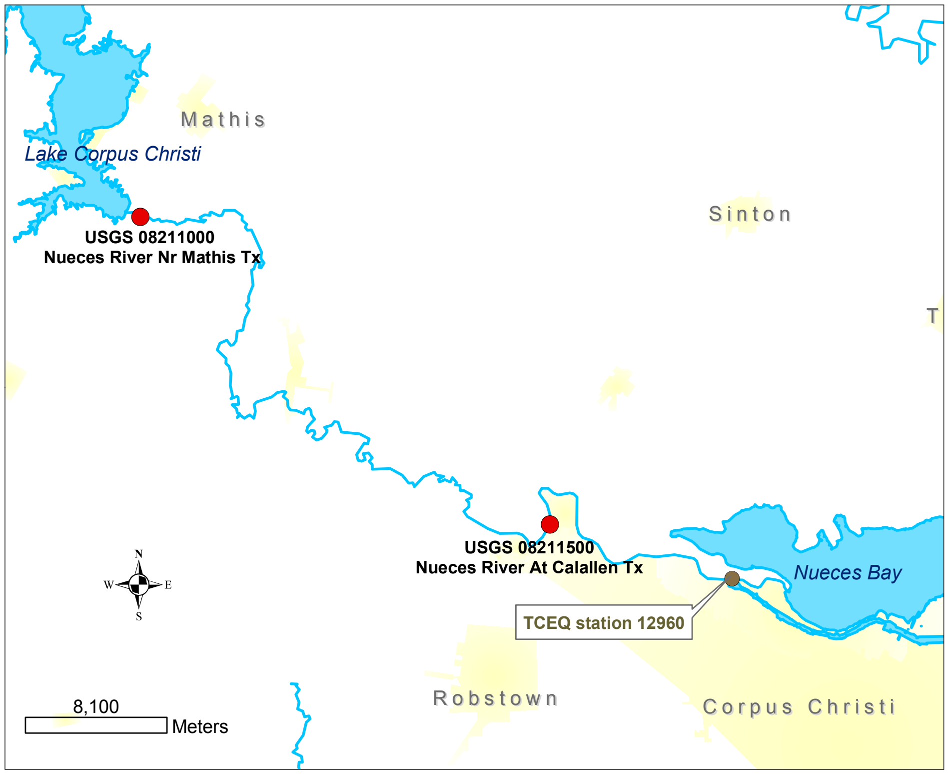


Figure 4.20 Map of Nueces Bay and Lake Corpus Christi with USGS and TCEQ monitoring stations

The zinc concentration in the lake is assumed to be constant downstream along Nueces River. The zinc loading from Lake Corpus Christi to Nueces Bay is then found by multiplying the zinc concentration in the lake by the inflow to the bay from the USGS gauging station at Callalen, TX.

The absence of data for total zinc in Lake Corpus Christi and in the Nueces River downstream suggests the use of natural background concentrations of zinc in water from the literature. From a Publication of the World Health

Organization, 2001 (Environmental health criteria; 221), some background zinc concentrations in fresh waters are given in Table 4.5. In 1981, Spear reported zinc concentrations that rarely exceed 40 μg/l in fresh waters (WHO, 2001). EPA reported in 1988 that concentrations of total zinc in uncontaminated fresh water are typically in the range of 0.5 to 10 μg/l. On the other hand, total zinc in Nueces River was measured in 1983 at the TCEQ monitoring station 12960 (Figure 4.20), and was found to be 21 μg/l. Therefore the concentration of total zinc in water assumed in Lake Corpus Christi for this study is estimated to be 20 μg/l.

Area	**Zinc concentration (μ g/l)**	**Reference**
Various rivers, worldwide	5–45[a]	Holland (1978)
Canada, unpolluted rivers and lakes	≤40	Spear (1981)
USA, nationwide	0.5–10	US EPA (1987)
USA, ambient surface water stations	20[b]	Eckel & Jacob (1988)

[a] Average
[b] Median

Table 4.5 Background zinc concentrations in freshwater systems (WHO, 2001)

4.3.3 Discharge from Inner Harbor via Central Power and Light

The Central Power and Light station is a Power plant that withdraws water from the Corpus Christi Inner Harbor channel for once through cooling water and discharges it to Nueces Bay through outfall 001. The existence of a direct transport of water from the contaminated Inner Harbor to Nueces Bay through the CP&L generating station means there is a point source load of zinc from the Inner Harbor's water to Nueces Bay.

The Texas Water Development Board (TWDB) conducted a study "Corpus *Christi Bay National Estuary Project"* (Matsumoto et al, 1997), to characterize the effects of recirculation of bay waters for industrial cooling on the circulation and salinity patterns of the CCBNEP study area. The TWDB used a circulation model TxBLEND, which is a 2-dimensional finite element model based on the generalized wave continuity equation, to study the effect of recirculating large volumes of bay water used for cooling of electric power generating plants. Two simulation periods were used, a dry period (1988-1989) and a wet period (1991-1992). Figure 4.21 shows the residual vectors for the existing conditions in the Nueces Bay, and figure 4.22 shows a snapshot of an animation showing the flow traces that were created by making the residual vectors move (Matsumoto et al, 1997). The residual vectors were computed by summing velocity vectors for the last 48 hours of the simulation period (Matsumoto et al, 1997).

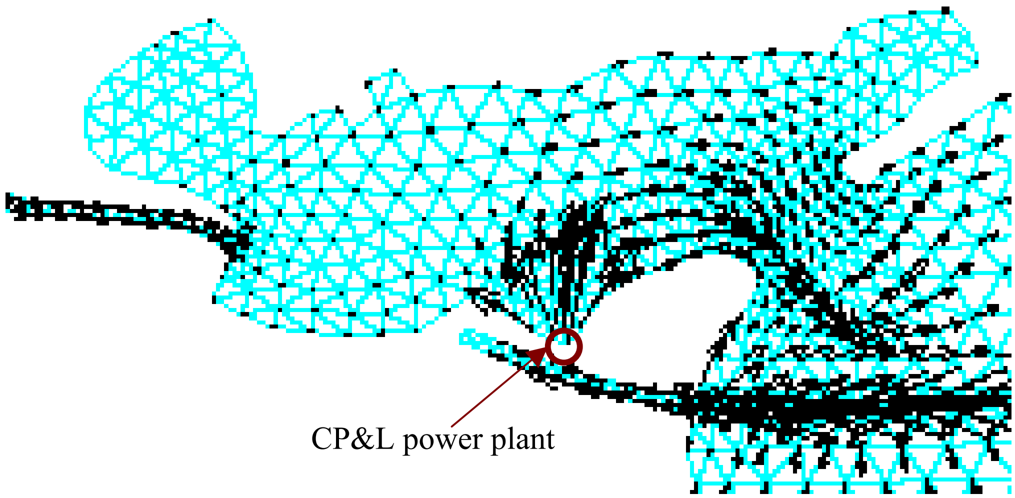


Figure 4.21 Residual vectors in Nueces Bay [source: TWDB]

Additional information on this study can be found online: http://hyper20.twdb.state.tx.us/data/bays_estuaries/ccbnep.html

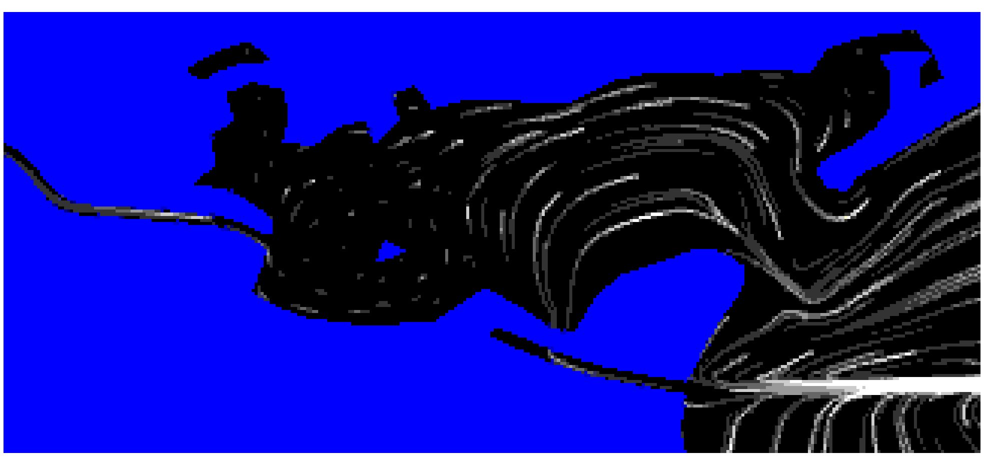


Figure 4.22 Snapshot of an animation showing the flow traces in Nueces Bay [source: TWDB]

As shown in Figures 4.21 and 4.22, the net flows coming from the Inner Harbor through the CP&L plant play a major role in recirulating and mixing Nueces Bay waters.

To account for zinc loadings from the Corpus Christi Inner Harbor channel, the ambient total zinc concentration in the channel is multiplied by the average amount of flow discharged to Nueces Bay via the CP&L station. The average total zinc concentration in the Inner Harbor is about 37 μg/l for the period 1982-2001 (Figure 4.23). The flow associated with this point source pollution is the CP&L average flow calculated in section 4.3.1.

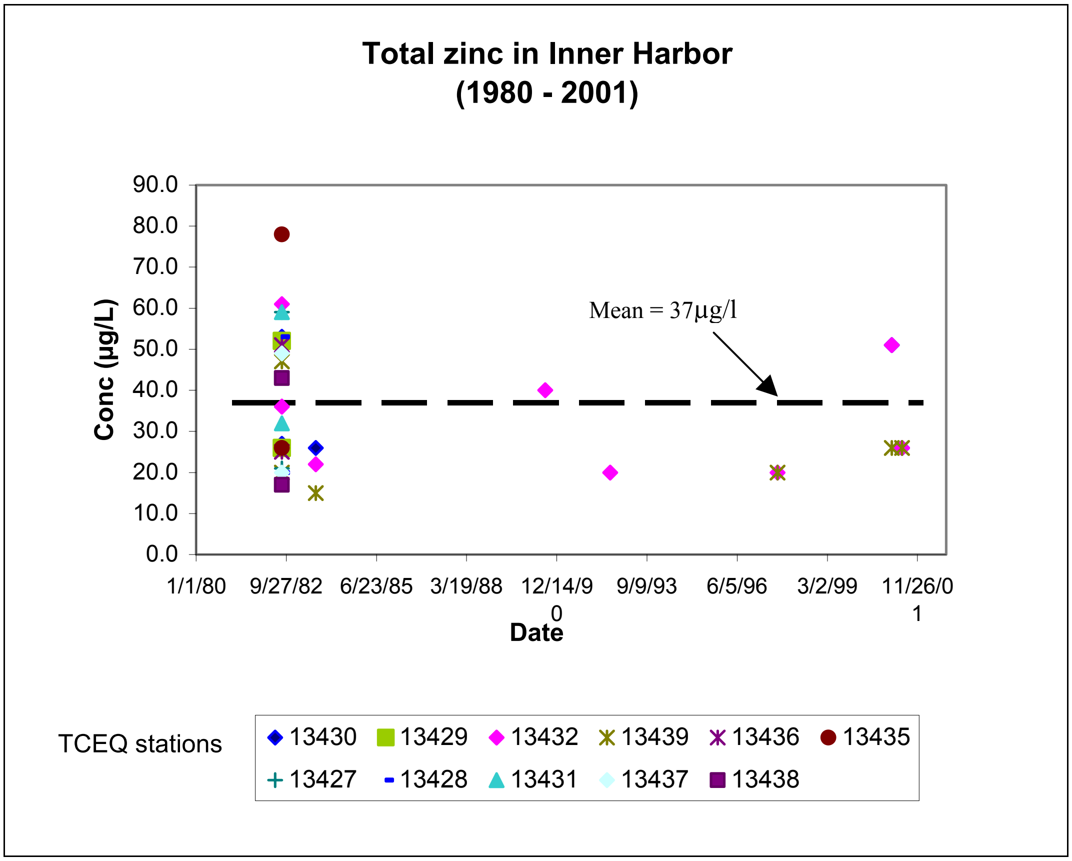


Figure 4.23 Total zinc concentrations in Inner Harbor (1982-2001)

4.4 LOADING MODEL

The major task is the development of a total loading model for Nueces Bay using a completely mixed system or continuously stirred tank reactor approach (CSTR). The CSTR is among the simplest approaches that can be used to model a natural water body. It is appropriate for a receiving water in which the contents are sufficiently well mixed as to be uniformly distributed (Chapra, 1997). The completely mixed assumption is justified for screening level analyses in the case of Nueces Bay since it is a shallow water body, where wind stress, tidal action and hydrodynamic circulation through water exchanged by the CP&L result in internal mixing of the bay waters. Figure 4.24 shows a representation scheme of the CSTR model.

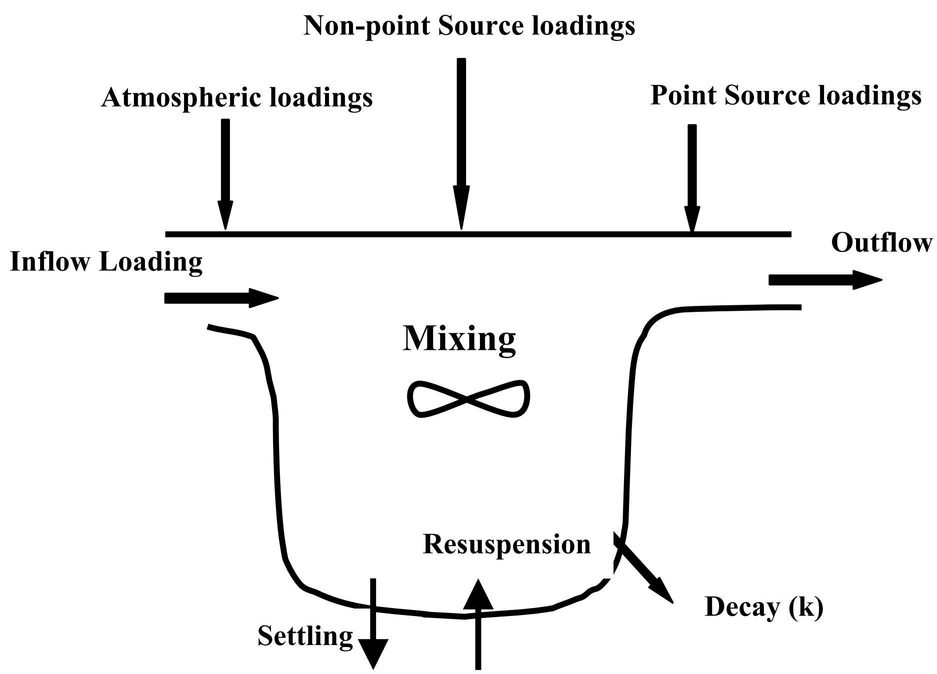


Figure 4.24 Continuously Stirred Tank Reactor representation (Chapra, 1997)

The exchange between the sediment and water layers is not taken into account in this screening level model. The water column and sediment layer in the bay system are assumed to have reached equilibrium, where settling of zinc sorbed in particles would be compensated by re-suspension from the bottom sediments.

The mass balance of total zinc for this well mixed Bay:

$$V\frac{dc}{dt} = W(t) - Qc - kVc$$

Where:

c: total zinc concentration in the bay ($M\ L^{-3}$)

k: decay coefficient (T^{-1})

V: volume of the bay (L^3)

W (t): loadings of zinc to the bay ($M^3\ T^{-1}$)

Q: outflow, sum of all flows coming to the bay ($L^3\ T^{-1}$)

If the system is subject to a constant loading W for a sufficient time, it will attain a dynamic equilibrium. At steady state, the concentration of zinc becomes:

$$c = \frac{W}{Q + kV}$$

Zinc has a negligible decay rate ($k \approx 0$); therefore, the equilibrium concentration of total zinc in Nueces Bay is given by:

$$c = \frac{W}{Q}$$

Two scenarios of total loadings are studied in this section. The first scenario includes all point sources and non-point sources of zinc loadings to Nueces Bay, except the loadings from Inner Harbor via CP&L station, and the second scenario includes all sources of loadings, with the load from Inner Harbor through CP&L station. The objective of these scenarios is to determine the weight and impact of the CP&L station in increasing zinc concentrations in Nueces Bay.

Chapter 5 – Results and discussion

5.1 RESULTS OF NON-POINT SOURCE LOADING CALCULATIONS

5.1.1 Land surface loading

For the land surface or watershed loadings, the resulting total runoff and total load of zinc are taken from the attribute table of the land cover layer *land_cov*, after vector calculation of runoff and load have been performed as explained in section 4.2.1. This resulting attribute table is shown in Table 5.1.

In ArcMap, the attribute table of *land_cov* is opened, and a right click on the runoff field *runoff_cms*, and load field *load_kg_perday* to select the function "Σ statistics" is made to open the statistical calculator of flow (Figure 5.1) and that of loads (Figure 5.2). This function gives the min, max, sum, mean and standard deviations of the column values. The sum value for the runoff and load columns represent the total runoff and zinc loads respectively. As a summary, the resulting watershed runoff and load of zinc from land surface pollution are:

Total runoff = Q_{wsh} = 1.83 m^3/s

Total load = W_{wsh} = 3.69 kg/day

Attributes of nlcd_cov

LAND_COVER_ID	GRID_CODE	Mean_preci	EMC	runoff	Runoff_cms	Load_kg_perday
1	82	787.4	16	66.560811	0.035279	0.048769
2	81	787.4	16	66.560811	0.000009	0.000013
3	81	787.4	16	66.560811	0.000002	0.000003
4	41	787.4	6	30.442503	0.000006	0.000003
5	51	787.4	6	30.442503	0.000014	0.000007
6	51	787.4	6	30.442503	0.000104	0.000054
7	71	787.4	6	30.442503	0.000001	0.000000
8	71	787.4	6	30.442503	0.000001	0.000000
9	71	787.4	6	30.442503	0.000001	0.000000
10	41	787.4	6	30.442503	0.000064	0.000033
11	71	787.4	6	30.442503	0.000001	0.000000
12	51	787.4	6	30.442503	0.000010	0.000005
13	41	787.4	6	30.442503	0.000001	0.000000
14	41	787.4	6	30.442503	0.000001	0.000000
15	71	787.4	6	30.442503	0.000001	0.000000
16	71	787.4	6	30.442503	0.000001	0.000000
17	41	787.4	6	30.442503	0.000003	0.000002
18	71	787.4	6	30.442503	0.000001	0.000000
19	41	787.4	6	30.442503	0.000001	0.000000
20	71	787.4	6	30.442503	0.000001	0.000000
21	51	787.4	6	30.442503	0.000008	0.000004
22	41	787.4	6	30.442503	0.000002	0.000001
23	71	787.4	6	30.442503	0.000001	0.000000
24	51	787.4	6	30.442503	0.000001	0.000000
25	71	787.4	6	30.442503	0.000053	0.000027
26	71	787.4	6	30.442503	0.000003	0.000001
27	71	787.4	6	30.442503	0.000002	0.000001
28	41	787.4	6	30.442503	0.000005	0.000003
29	81	787.4	16	66.560811	0.000008	0.000011
30	71	787.4	6	30.442503	0.000002	0.000001
31	51	787.4	6	30.442503	0.000002	0.000001
32	51	787.4	6	30.442503	0.000006	0.000003
33	51	787.4	6	30.442503	0.000001	0.000000
34	71	787.4	6	30.442503	0.000001	0.000000
35	81	787.4	16	66.560811	0.000002	0.000003
36	41	787.4	6	30.442503	0.000001	0.000000
37	51	787.4	6	30.442503	0.000004	0.000002
38	81	787.4	16	66.560811	0.000004	0.000005
39	51	787.4	6	30.442503	0.000001	0.000000
40	51	787.4	6	30.442503	0.000004	0.000002
41	51	787.4	6	30.442503	0.000011	0.000006
42	71	787.4	6	30.442503	0.000004	0.000002

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Table 5.1 Vector calculation table of runoff and zinc loads from each land cover polygon

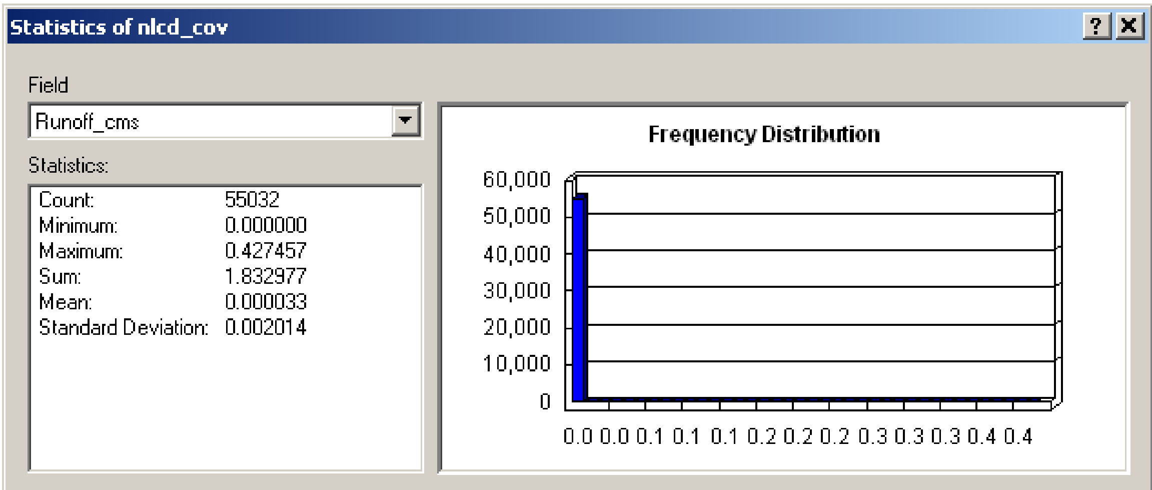


Figure 5.1 Statistical calculator of runoff (m^3/s) values

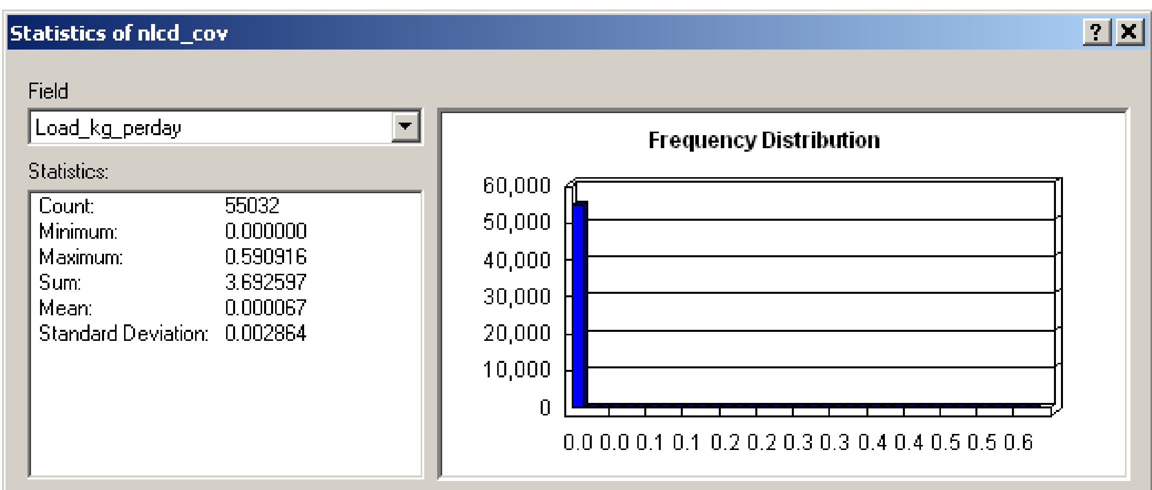


Figure 5.2 Statistical calculator of values for zinc loads

5.1.2 Atmospheric deposition

The total atmospheric deposition measured at the White Point station is 91 kg/km^2-yr. The atmospheric load to the study area is applied to Nueces Bay only because it is already accounted for on the land surface by the EMC values. With an average area of 74.87 km^2, the average atmospheric deposition of zinc in Nueces Bay is obtained by multiplying the atmospheric deposition at White Point (91 kg/km^2-yr) by the bay surface area (74.87 km^2). The resulting atmospheric zinc load is W_{at} = 18.67 kg/d.

5.2 RESULTS OF POINT SOURCE LOADINGS CALCULATION

5.2.1 Permitted dischargers

As discussed in section 4.3.1 of chapter 4, the total flow and zinc loads from the permitted dischargers are summarized below:

Total Flow = Q_{pd} = 16.55 m^3/s

Total load = W_{pd} = 0.71 kg/d

5.2.2 Lake Corpus Christi

For the contribution of Lake Corpus Christi as a point source load, the flow entering Nueces Bay is the Nueces river inflow as measured in USGS 08211500, Nueces River at Callalen station. The average stream flow in this station between 1991 and 2000 is 2.47m^3/s (USGS, 2000). The zinc load from lake Corpus Christi is found by multiplying the total zinc concentration in the lake (20μg/l) by the Nueces River flow (see section 4.3.2 for details). The resulting flow and zinc loads are:

Flow = Q_{LCC} = 2.47 m^3/s

Load = W_{LCC} = 4.27 kg/d

5.2.3 Load from Inner Harbor via Central Power and Light station

As discussed in section 4.3.3, the total load of zinc coming from the Inner Harbor through CP&L station is found by multiplying the zinc concentration in Inner Harbor (37μg/l) by the average flow discharged by the plant (16.5 m^3/s). The resulting zinc load is:

$W_{CP\&L}$ = 52.75 kg/d

5.3 TOTAL LOADING MODEL RESULTS

5.3.1 CSTR without Inner Harbor load through CP&L station

Figure 5.3 shows the loadings for scenario 1. All point and non-point source loadings of zinc, established in previous sections, are included except for the load from Inner Harbor through the Central Power and Light (CP&L) station. The outflow Q_T is equal to the sum of the inflows, and the total zinc load W_T is equal to the sum of non-point and point source loads.

$W_T = W_{wsh} + W_{at} + W_{LCC} + W_{pd} = 3.69 + 18.67 + 4.27 + 0.71 = 27.34$ kg/d

$Q_T = Q_{wsh} + Q_{LCC} + Q_{pd} = 1.83 + 2.47 + 16.55 = 20.85$ m^3/s

The steady state concentration of total zinc (c_1) in Nueces Bay is:

$$c_1 = \frac{W_T}{Q_T} = \frac{27.34(kg/d)*10^9(\mu g/kg)}{20.85(m^3/s)*10^3(L/m^3)*86400(s/d)} = 15.18\mu g/L$$

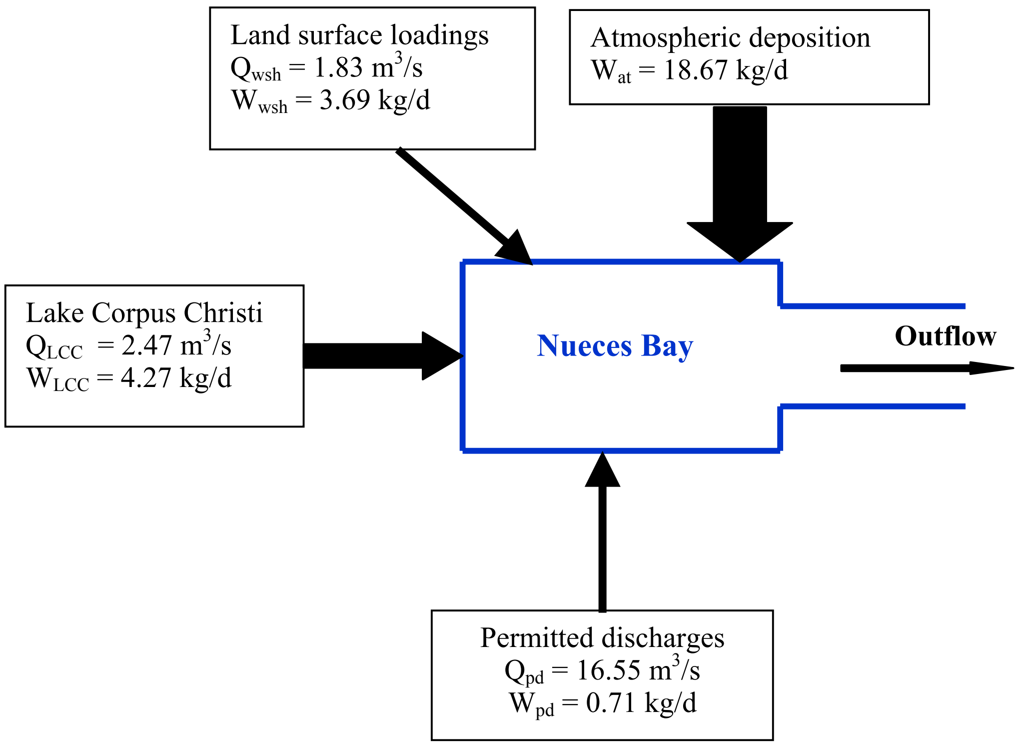


Figure 5.3 Loading model for Nueces Bay without Inner harbor load via CP&L station

4.4.2 CSTR with Inner Harbor load through CP&L station

Scenario 2 of the CSTR model accounts for loadings from Inner Harbor discharged by the CP&L station (Figure 5.4).

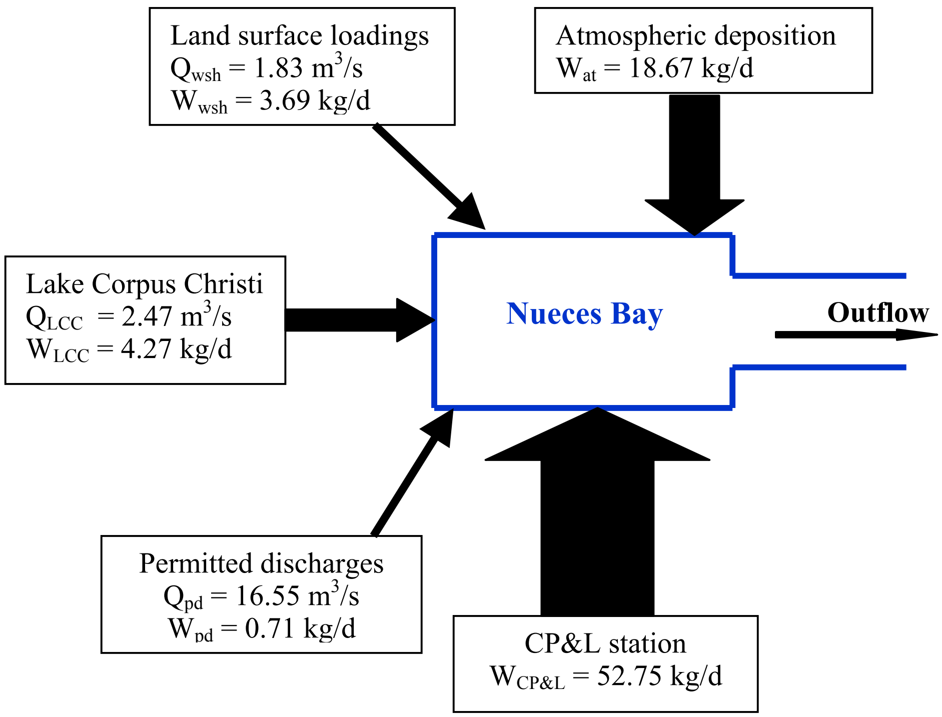


Figure 5.4 Loading model for Nueces Bay with Inner Harbor load through CP&L station

The Total flow and zinc loads for this model are:

$W_T = W_{wsh} + W_{at} + W_{LCC} + W_{pd} + W_{CP\&L} = 3.69 + 18.67 + 4.27 + 0.71 + 52.75 =$ 80.1 kg/d

$Q_T = Q_{wsh} + Q_{NR} + Q_{pd} + Q_{CP\&L} = 1.83 + 2.47 + 16.55 = 20.85\ m^3/s$

The steady state concentration of total zinc (c_2) in the bay is:

$$c_2 = \frac{W_{Total}}{Q_T} = \frac{80.1(kg/d) * 10^9 (\mu g/g)}{20.85(m^3/s) * 10^3 (L/m^3) * 86400(s/d)} = 44.46 \mu g/L$$

5.4 Discussion

Non-point source pollution contributes of about 22.36 kg/d of zinc loadings to Nueces Bay. 16.4 % (3.69 kg/d) of this total load is attributed to land surface runoff, whereas 83.5 % (18.67 kg/d) is attributed to atmospheric deposition. The atmospheric load was only applied to the bay area since the EMC values are assumed to account for the atmospheric load over the watershed land surface. However, the atmospheric deposition over the bay is five times higher than the land surface load. In addition, there is an uncertainty over the use of EMC values for load estimation, and how accurately they represent constituent concentrations over the land surface.

The total Point Source pollutant load is 57.73 kg/d, with the largest load coming from the Inner Harbor via the CP&L discharge. The Nueces River load of zinc from Lake Corpus Christi is approximately 4.27 kg/d, which is comparable to land surface loads. Permitted discharger loads of zinc represent the smallest load contribution, with an approximate zinc load of 0.7 kg/d.

The total loads of zinc originating from both point source and non-point source pollutants are around 80 kg/d. Figure 5.5 shows the partitioning of this total load between all the individual pollution sources studied in this project. The largest contribution of zinc is the Inner Harbor loads through the Central Power and Light generating station, which represent 66% of the total load. The second largest zinc source load is atmospheric deposition (23 %). Land surface and Lake Corpus Christi have little impact on the total loading and represent each 5 % of the total load, whereas only 1% of the load is attributed to point source permitted dischargers.

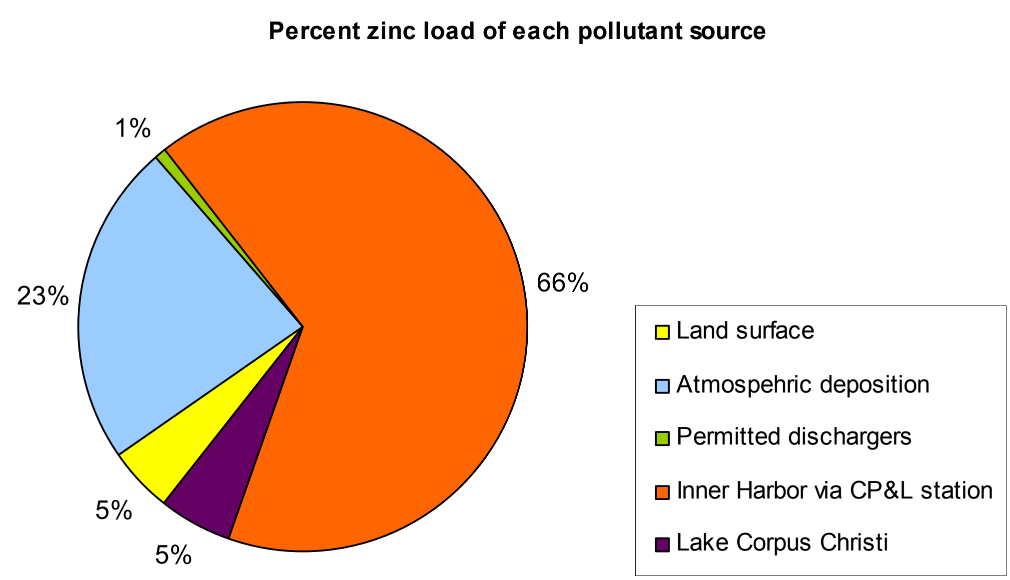


Figure 5.5 Percent of each zinc loading source to Nueces Bay

The CP&L cooling water represent the largest contribution of inflow to Nueces Bay with 79 % of the total flow, followed by Nueces river inflow (12 %)

and Land surface runoff (9 %) (Figure 5.6). The municipal flow is almost undetectable with 0.2 % of the total flow to the bay.

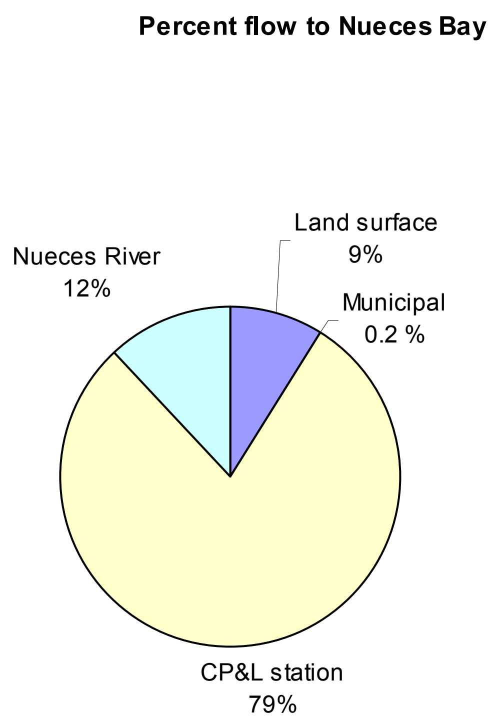


Figure 5.6 Percent flows to Nueces Bay

The average measured concentration of total zinc in Nueces Bay is about 46.8 μg/l for the period 1980-1988. The two scenarios of CSTR models were run to simulate expected concentrations of total zinc in Nueces Bay. The first scenario, excluding the Inner Harbor load input by CP&L station, gives an equilibrium concentration of total zinc of 15.18 μg/l, which is three times lower than the mean observed concentration. The second CSTR model, taking into account loads coming from Inner Harbor channel through the CP&L electric station, resulted in an equilibrium concentration of zinc equal to 44.46 μg/l. This concentration is very close to the average observed concentration. Figure 5.7 compares the equilibrium total zinc concentrations simulated by both scenarios of the CSTR model to the observed concentrations in the bay.

The CSTR modeling clearly shows a significant difference in simulated concentrations between scenario 1 and 2. The first scenario underestimates total zinc concentrations, whereas the second model gives better results with concentration comparable to what is measured. This modeling process shows that the direct transport of water from the Inner Harbor to Nueces Bay through Central Power and Light station has a significant impact on the water quality in Nueces Bay. Furthermore, this point-loading source is likely to be an important component responsible for maintaining zinc impairment in Nueces Bay.

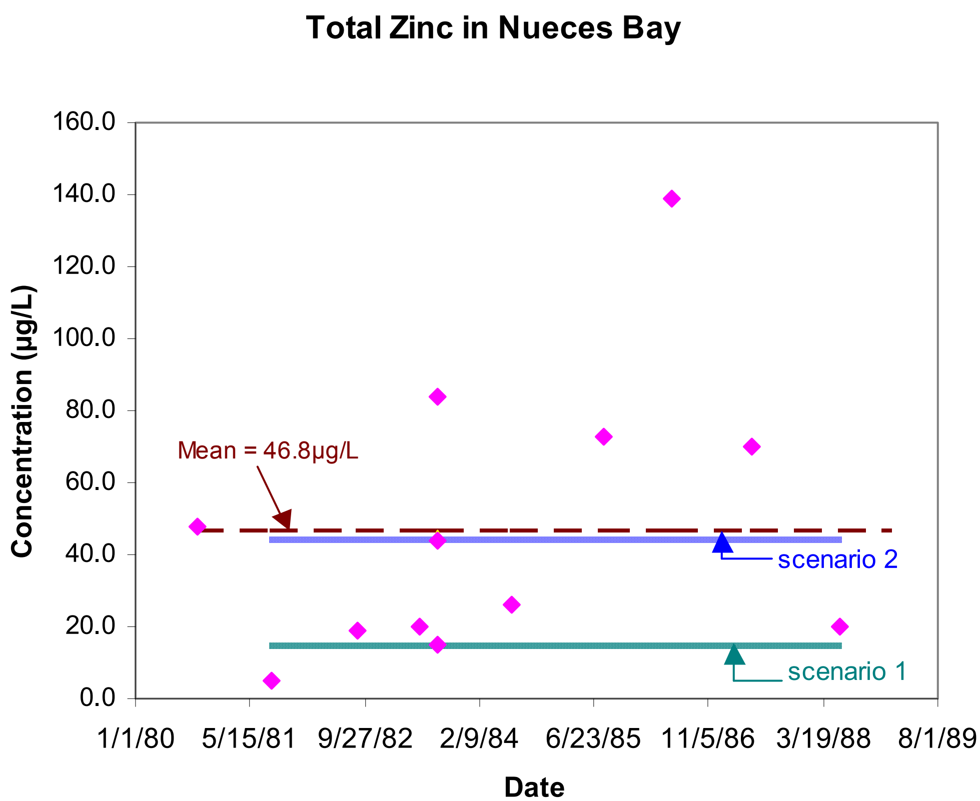


Figure 5.7 Equilibrium concentrations of zinc for CSTR model scenarios and their comparison with measured total zinc in Nueces Bay

Chapter 6 – Conclusions and Recommendations

6.1 CONCLUSIONS

The overall objective of this project is to provide assistance and support to TCEQ in its effort to develop a Total Maximum Daily Load (TMDL) for zinc in Nueces Bay that will support oyster water use. Many studies have been done in the larger area of the Corpus Christi Bay complex. The Coastal Bend Bays and Estuaries Program initiated studies to identify point (Armstrong and Ward, 1998) and non-point sources of pollution (Baird *et al.*, 1996), quantify atmospheric deposition (Wade *et al.*, 2000), model total loads to Nueces Bay (Quenzer *et al*, 1998), monitor water and sediment quality (Carr et al., 1998), and compile and analyze historical water, sediment and tissue data (Ward and Armstrong, 1997). These studies, along with other sources of information served as the basis for this TMDL project.

Information and data about zinc concentrations in water and sediments, and contributing point and non-point sources of zinc in Nueces Bay, were compiled and analyzed. Data concerning zinc levels observed in fish tissue were also compiled from the Texas Department of Health. Additional data necessary for watershed processing and non-point source estimation were also assembled (geospatial data, land use/ land cover, EMC values). A simple water quality model of total zinc in the water column was established using mass balance approach, and expected equilibrium concentrations were derived.

The monitoring zinc data in Nueces Bay were very limited and sparse to establish a general trend. In particular, total zinc data were insufficient and only available for the period 1980-1988. The mean concentration of total zinc during this period is 46.8 μg/l, which is much higher than background concentrations in seawaters. No recent data has been measured for total zinc in Nueces Bay after 1988, which is very limiting to the analysis of contamination patterns in the bay. In addition, there exists the potential that samples for zinc analyses may have been contaminated during field and laboratory procedures for handling and analyzing samples. In Nueces Bay, the average concentration of dissolved zinc measured with the conventional sampling method during the period 1999-2001 was 3 times higher than the one measured with the ultra-clean method. Consequently, historical zinc data obtained from TCEQ are likely to overestimate the metal concentrations, and therefore there is a significant need for more zinc monitoring data sampled with the clean methods. As for the sediment data, the mean zinc concentration during for the period 1980-2002 is about 100 mg/kg, which exceeds the background zinc concentration of 90 mg/kg established by EPA (1977).

Geographic Information System (GIS) tools and applications were used to delineate the watershed draining to Nueces Bay, and resulted in a drainage area of 935.5 Km^2 (≈ 231,167 acres). Furthermore, vector calculations were performed in GIS environment to estimate flows and zinc load from non-point source watershed loading. This estimation resulted in a surface runoff of 1.83 m^3/s and land surface zinc loads of 3.69 kg/d. Atmospheric deposition is part of the non-point source pollution and contributes 18.67 kg/d of zinc load to Nueces Bay. Point source pollution includes Nueces river discharge from Lake Corpus Christi, Inner Harbor discharge through the CP&L station, and TCEQ permitted municipal and industrial dischargers, including cooling water dischargers. Non-permitted dischargers were not included because of their minimal contribution (Armstrong et al, 1997).

Table 6.1 gives a summary of the zinc loading estimation. The water withdrawn from Inner Harbor by the CP&L station contributes with a zinc load of 52.75 kg per day, which constitutes the largest load of zinc (66 %) to Nueces Bay. The second largest zinc load (23 %) is attributed to atmospheric deposition. With only 5% of the total loads, Lake Corpus Christi and land surface have little impact on water quality of the bay. Furthermore, loads from point source permitted dischargers are barely detectable, representing 1 % of the total loads.

Pollution source	Loads (kg/d)	Percent (%)
Land surface	3.69	5
Atmospheric deposition	18.67	23
Permitted dischargers	0.71	1
Inner Harbor discharge via CP&L station	52.75	66
Lake Corpus Christi	4.27	5

Table 6.1 Zinc loading from each pollution source

The most important flow coming to Nueces Bay is the CP&L cooling water withdrawn from Inner Harbor, which equals 16.5 m^3/s (Table 6.2). This flow constitutes 79 % of the Total inflow to the bay and is 7 times higher than the Nueces River flow (2.47 m^3/s). The second largest flow to Nueces Bay is the

Nueces River with 12 % of the total flow, followed by land surface runoff constituting 9 % of the total inflow (Table 6.2).

Pollution source		Flow (m^3/s)	Percent (%)
Land surface		1.83	9
Permitted dischargers	Municipal	0.05	0.2
	CP&L station	16.5	79
Nueces River		2.47	12

Table 6.2 Flows to Nueces Bay

A simple water quality model (Continuously Stirred Tank Reactor) was used to simulate equilibrium concentrations of total zinc in Nueces Bay. This Continuous Stirred Tank Reactor (CSTR) model assumes that Nueces Bay is a completely mixed reactor where input loads are dumped and mixed in the bay. Two CSTR model scenarios were performed. Loads from the Inner Harbor discharged by CP&L station were disregarded in scenario 1, whereas they were included in scenario 2. Expected total zinc concentration from scenario 1 was very low compared to the mean observed concentration, whereas expected equilibrium concentration from scenario 2 was comparable to the average observed zinc concentration for the period 1980-1988.

Since the major source of zinc loadings in Nueces Bay is the water discharged from the Inner Harbor, and based on the results of the CSTR model, one hypothesis can be made to stipulate that elevated zinc levels in Nueces Bay may be due to discharges from the Inner Harbor via the CP&L generating station. The 2002 oysters sampling results support this hypothesis since average zinc concentration in oysters collected from the site near CP&L station was 1486 mg/kg edible tissue, while it was only 770 mg zinc/kg edible tissue at the causeway site.

The CP&L Nueces generating station continuously circulates a flow at a an approximate nominal rate of 16.5 m^3/s, which is around 7 times higher than the mean inflow of the Nueces River as measured in USGS station near Callalen. Therefore, the CP&L plant plays a major role in recirculating and mixing Nueces Bay waters. Consequently, the question of whether Nueces Bay water quality will improve once CP&L Power Plant discontinues operation still needs to be investigated.

In interpreting results of this study, it should be noted that there are several uncertainties related to data origin, loading calculations and modeling process. Some of these uncertainties are inherent to errors in reporting zinc monitoring data or contamination of samples for zinc testing during handling or field analysis. The accuracy of EMC values used in estimating the land surface loadings is also uncertain. In addition, loads calculated for Lake Corpus Christi were based on the assumption that concentration of total zinc in the lake is similar to background concentrations. Also, the use of Typical Pollutant Concentrations (TPCs) taken from the study by Armstrong et al (1997) have some uncertainty due to the nature of their development. Moreover, the lack of self-reporting zinc data from permitted dischargers may have caused an underestimation of point source pollutant loads.

6.2 RECOMMENDATIONS

The following recommendations can be submitted:

- The most important source of zinc contamination in Nueces Bay is the Central Power and Light station's water discharge from the Corpus Christi Inner Harbor. The potential danger that the Power plant continues to contaminate Nueces Bay should be further investigated by collecting water samples from the cooling water discharged by the station, and areas in Nueces Bay most impacted by this discharge.
- More intensive sampling of total zinc in waters and sediments of Nueces Bay should be undertaken to determine the geographic and temporal extent of zinc contamination in the bay, and verify the current high concentrations.
- Collect additional metals (total and dissolved) in water and sediment using clean methods in both the Inner Harbor and Nueces Bay to increase the reliability of the model results. Also, with regards to the sediment data, it would be useful to stratify the sediment core into upper, middle and lower sections prior to analysis to determine if the historical zinc loads have been buried with new sediment.
- Determine the impact (positive or negative) to water quality in Nueces Bay and Inner Harbor if CP&L station discontinues operation. If CP&L station is the major source of zinc loadings to Nueces Bay, then one should address questions like: how long it will take after the power plant cease operation before improvements in water quality, and ultimately in

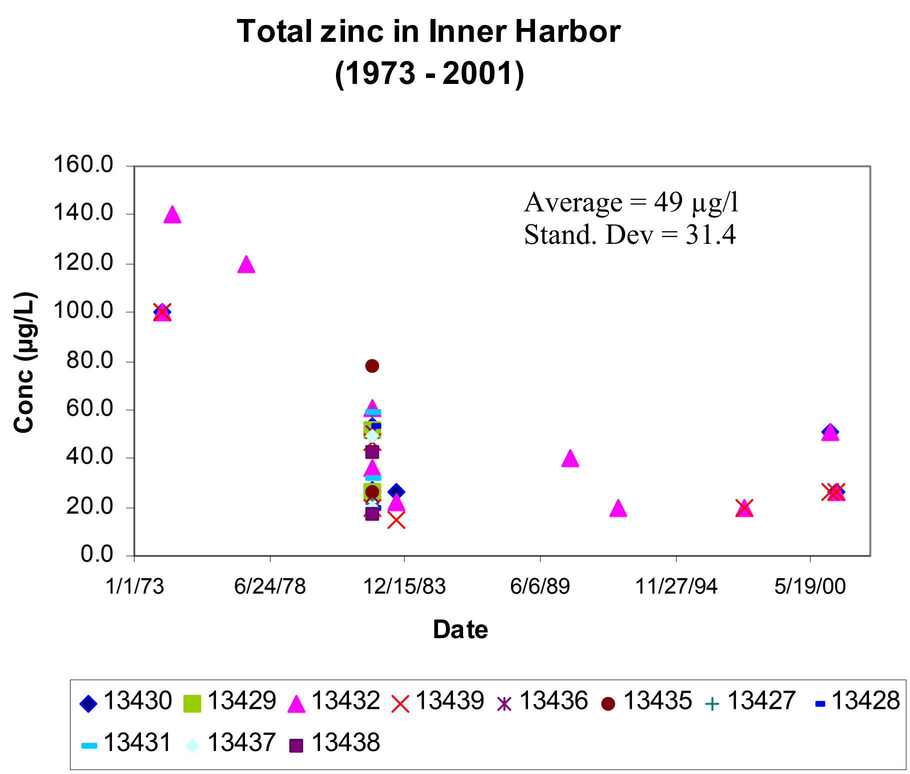
oyster tissue of Nueces Bay, are visible? When can we expect to see attainment of the water quality standard?

- Atmospheric load of zinc is significant; therefore specific sources of atmospheric deposition of zinc to the bay should be determined. Wind-blown materials from the adjacent dredge disposal sites, which contain material dredged from the Inner Harbor, may be one of the sources. The impact of dredging activities in the Corpus Christi Inner Harbor should be investigated.
- The Continuously Stirred Tank Reactor (CSTR) is an idealized well-mixed system that doesn't account for water-sediment exchange or metal partitioning into the dissolved and particulate phase. A more elaborate model such as the Toxics Model (see Appendix E) considering surface water underlain by a well-mixed active sediment layer, where the resulting concentrations are attained by direct analytical solutions both at steady state and time-variable conditions.

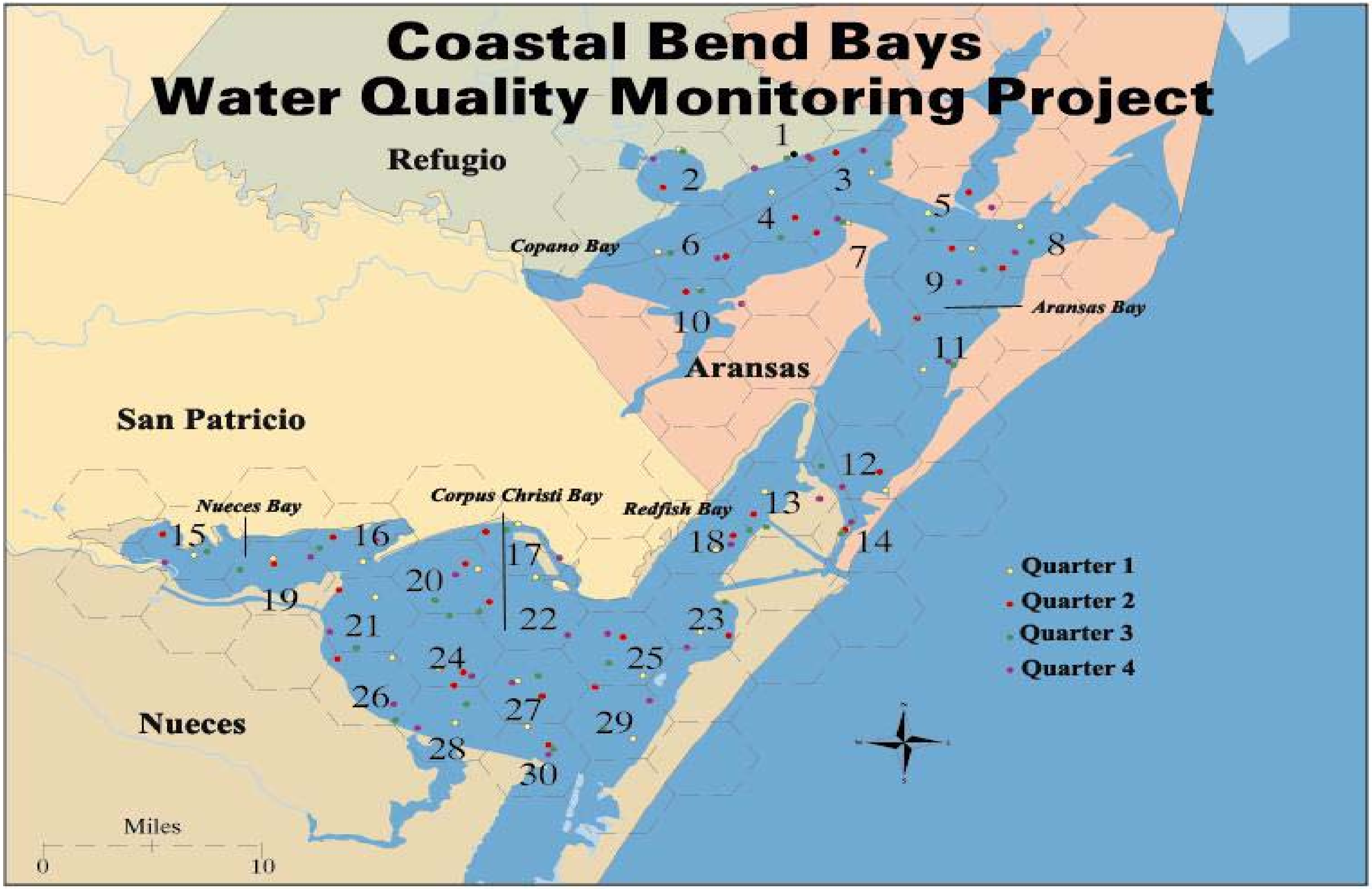
Appendix A: Total zinc concentrations in stations within the Corpus Christi Inner Harbor for the period 1974 – 2001

Station	Date	Total zinc (µg/l)
13427	8/10/1982	21.0
13427	8/10/1982	59.0
13428	8/10/1982	20.0
13428	8/10/1982	53.0
13429	8/10/1982	26.0
13429	8/10/1982	52.0
13430	2/21/1974	100.0
13430	2/21/1974	100.0
13430	8/10/1982	27.0
13430	8/10/1982	53.0
13430	8/19/1983	26.0
13430	2/13/2001	51.0
13430	6/7/2001	26.0
13431	8/10/1982	32.0
13431	8/10/1982	59.0
13432	2/21/1974	100.0
13432	2/21/1974	100.0
13432	7/12/1974	140.0
13432	7/5/1977	120.0
13432	8/10/1982	36.0
13432	8/10/1982	61.0
13432	8/19/1983	22.0
13432	8/8/1990	40.0
13432	7/28/1992	20.0
13432	8/27/1997	20.0
13432	2/13/2001	51.0
13432	6/7/2001	26.0
13433	8/10/1982	32.0
13433	8/10/1982	75.0
13434	8/10/1982	37.0
13434	8/10/1982	55.0
13435	8/10/1982	26.0
13435	8/10/1982	78.0
13436	8/10/1982	25.0
13436	8/10/1982	51.0
13437	8/10/1982	20.0
13437	8/10/1982	49.0
13438	8/10/1982	17.0
13438	8/10/1982	43.0
13439	2/21/1974	100.0

13439	2/21/1974	100.0
13439	8/10/1982	20.0
13439	8/10/1982	47.0
13439	8/19/1983	15.0
13439	8/27/1997	20.0
13439	2/13/2001	26.0
13439	6/7/2001	26.0



Appendix B: Sampling sites in the coastal Bend Bay Water Monitoring Program (CCBNEP)


Coastal Bend Bays
Water Quality Monitoring Project
Refugio
Copano Bay
Aransas Bay
Aransas
San Patricio
Nueces Bay
Corpus Christi Bay
Redfish Bay
Nueces
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Appendix C: Dissolved zinc in the Corpus Christi Inner Harbor

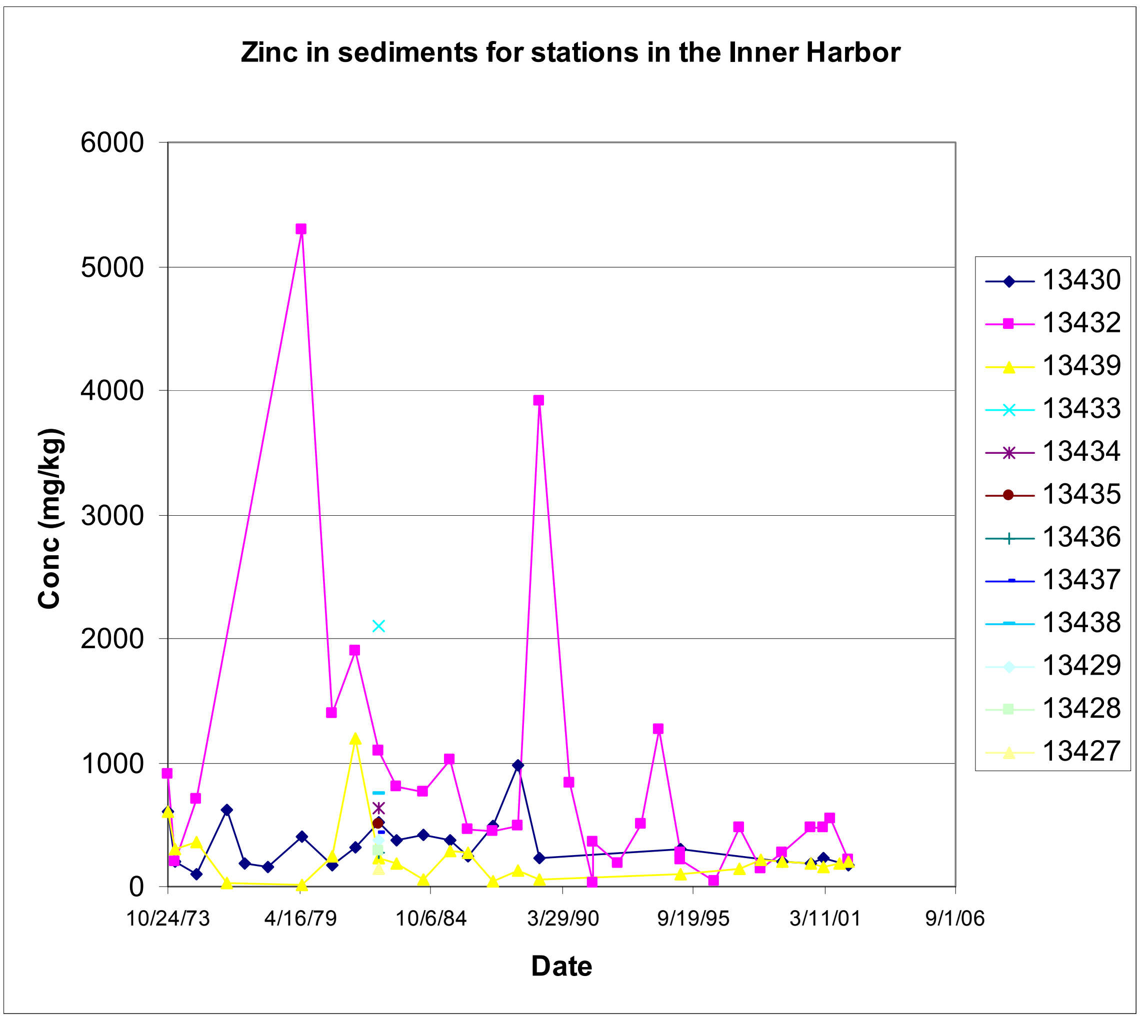
Station	Date	Dissolved zinc (μg/l)
13430	5/14/1998	11.0
13430	7/21/1998	5.0
13430	11/17/1998	25.0
13430	2/8/1999	8.0
13430	4/19/1999	8.0
13430	6/22/1999	8.0
13430	8/28/2000	16.0
13430	2/13/2001	32.0
13430	6/7/2001	8.0
13432	8/8/1990	40.0
13432	7/10/1991	20.0
13432	7/28/1992	40.0
13432	8/4/1993	5.0
13432	4/27/1994	25.0
13432	3/23/1995	3.0
13432	8/13/1996	3.0
13432	8/27/1997	4.0
13432	5/14/1998	10.0
13432	7/21/1998	7.0
13432	11/17/1998	34.0
13432	2/8/1999	8.0
13432	4/19/1999	12.0
13432	6/22/1999	9.0
13432	8/28/2000	16.0
13432	2/13/2001	32.0
13432	6/7/2001	8.0
13439	8/27/1997	4.0
13439	5/14/1998	5.0
13439	7/21/1998	5.0
13439	11/17/1998	22.0
13439	2/8/1999	8.0
13439	4/19/1999	8.0
13439	6/22/1999	8.0
13439	8/28/2000	16.0
13439	2/13/2001	33.0
13439	6/7/2001	8.0
13439	10/31/2001	16.0

Appendix D: Zinc in sediments in the Inner Harbor (1973-2002)

Station	Date	Zinc in sediments (mg/kg)
13427	8/10/1982	140.0
13428	8/10/1982	290.0
13429	8/10/1982	370.0
13430	10/24/1973	600.0
13430	2/21/1974	200.0
13430	1/15/1975	100.0
13430	4/6/1976	620.0
13430	1/5/1977	180.0
13430	12/28/1977	164.0
13430	5/15/1979	400.0
13430	8/26/1980	170.0
13430	8/13/1981	310.0
13430	8/10/1982	520.0
13430	8/10/1982	520.0
13430	5/4/1983	370.0
13430	6/26/1984	420.0
13430	8/6/1985	370.0
13430	5/1/1986	247.0
13430	5/5/1987	484.0
13430	5/23/1988	980.0
13430	4/24/1989	230.0
13430	3/6/1995	302.0
13430	6/22/1999	206.0
13430	8/28/2000	194.0
13430	2/13/2001	229.0
13430	3/11/2002	178.0
13431	8/10/1982	520.0
13432	10/24/1973	900.0
13432	2/21/1974	200.0
13432	1/15/1975	700.0
13432	5/15/1979	5300.0
13432	8/26/1980	1400.0
13432	8/13/1981	1900.0
13432	8/10/1982	1100.0
13432	8/10/1982	1100.0
13432	5/4/1983	800.0
13432	6/26/1984	760.0
13432	8/6/1985	1020.0
13432	5/1/1986	454.0

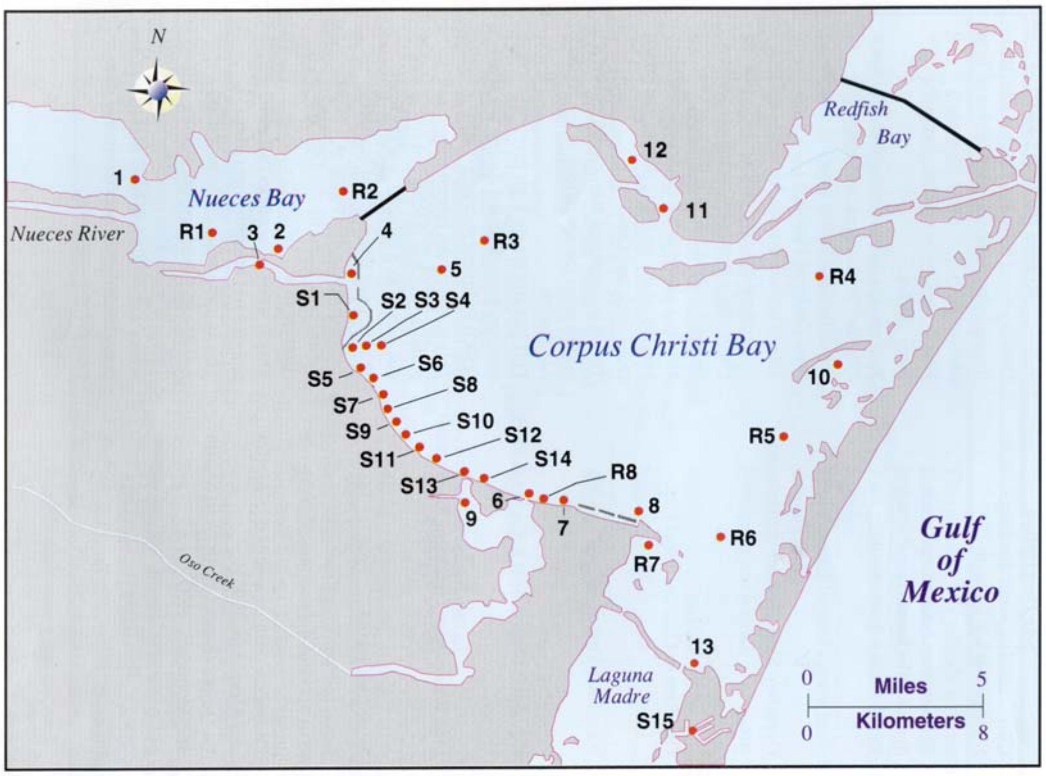
13432	5/5/1987	441.0
13432	5/23/1988	490.0
13432	4/24/1989	3920.0
13432	8/8/1990	830.0
13432	7/10/1991	23.0
13432	7/10/1991	366.0
13432	7/28/1992	186.0
13432	8/4/1993	506.0
13432	4/27/1994	1260.0
13432	3/6/1995	278.0
13432	3/23/1995	214.0
13432	8/13/1996	41.0
13432	8/27/1997	473.0
13432	7/21/1998	144.0
13432	6/22/1999	276.0
13432	8/28/2000	475.0
13432	2/13/2001	474.0
13432	6/7/2001	545.0
13432	3/11/2002	212.0
13433	8/10/1982	2100.0
13434	8/10/1982	640.0
13435	8/10/1982	510.0
13436	8/10/1982	280.0
13437	8/10/1982	430.0
13438	8/10/1982	750.0
13439	10/24/1973	600.0
13439	2/21/1974	300.0
13439	1/15/1975	360.0
13439	4/6/1976	34.0
13439	5/15/1979	9.0
13439	8/26/1980	240.0
13439	8/13/1981	1200.0
13439	8/10/1982	230.0
13439	8/10/1982	230.0
13439	5/4/1983	180.0
13439	6/26/1984	58.0
13439	8/6/1985	290.0
13439	5/1/1986	269.0
13439	5/5/1987	42.0
13439	5/23/1988	130.0
13439	4/24/1989	61.0
13439	3/23/1995	105.0

13439	8/27/1997	140.0
13439	7/21/1998	214.0
13439	6/22/1999	197.0
13439	8/28/2000	190.0
13439	2/13/2001	161.0
13439	10/31/2001	187.0
13439	3/11/2002	198.0



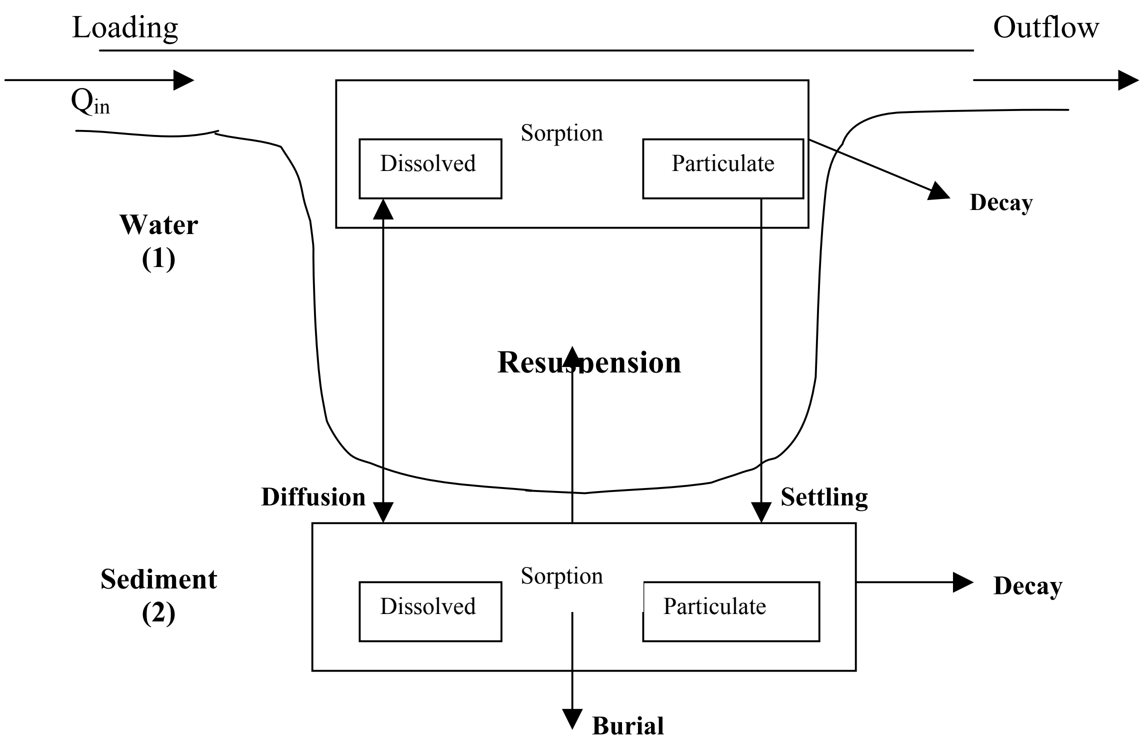
Appendix E: Sediment zinc data from Carr et al (1998)

Station	Zinc (mg/kg dry weight)
1	99.81
2	32.01
3	54.36
4	110.93
5	95.17
6	38.42
7	5.19
8	44.73
9	41.06
10	13.18
11	15.49
12	30.96
13	8.71
S1	301.35
S2	24.44
S3	20.69
S4	65.52
S5	12.17
S6	10.78
S7	12.07
S8	16.75
S9	23.14
S10	11.28
S11	8.82
S12	11.68
S13	8.84
S14	12.29
S15	25.97
R1	146.45
R2	134.07
R3	112.69
R4	61.07
R5	23.05
R6	8.79
R7	74.13
R8	21.61



Location of sampling sites in the Corpus Christi Bay National Estuary Program (Carr et al, 1998)

Appendix F: Toxics Model (Chapra, 1997)



Metal budget for a well-mixed bay with sediment feedback (Chapra, 1997)

There is an inflow rate Q_{in} with a contaminant concentration c_{in} and an outflow rate. The contaminant is partitioned into particulate and dissolved fraction. The particulate fraction is subject to settling, resuspension and burial with velocities of v_s, v_r and v_b, while the dissolved fraction could volatilize across the air-water interface (neglected), and diffuse between water column and sediment layer with diffusive mixing velocity.

$$V_1 \frac{dc_1}{dt} = Qc_{in} - Qc_1 - v_s AF_{p1}c_1 + v_r Ac_2 + v_d A(F_{d2}c_2 - F_{d1}c_1)$$

$$V_1 \frac{dc_2}{dt} = v_s AF_{p1}c_1 - v_r Ac_2 - v_b Ac_2 + v_d A(F_{d1}c_1 - F_{d2}c_2)$$

At steady state, these equation can be solved for :

$$c_1 = \frac{Qc_{in}}{Q + v_T A}$$

$$v_2 = \frac{v_s F_{p1} + v_d F_{d1}}{(1-\phi)\rho(v_r + v_b + v_d F_{d2})} c_1$$

Where v_T = net loss rate (m yr^{-1})

$$v_T = (1 - F_r^{'})(v_s F_{p1} + v_d F_{d2})$$

And $$F_r^{'} = \frac{v_r + v_d F_{d2}}{v_r + v_b + v_d F_{d2}}$$

t = time (d)
c = concentration (μg/L)
v = volume (m^3)
c_{in} = inflow concentration (μg/L)
k = first order decay coefficient, negligible
A = sediment surface area (m^2)
vs = settling velocity of solids (m d^{-1})
v_d = sediment-water diffusion mass transfer coefficient (m d^{-1})
v_r = resuspension velocity (m d^{-1})

v_b = burial velocity (m d^{-1})
ρ = Sediment density (g/m^3)
ϕ = Sediment porosity
m = suspended solids concentration (g/m^3)

The dissolved and particulate fractions are:

$$F_{d1} = 1 - F_{p1} = \frac{1}{1 + K_{d1} m}$$

$$F_{d2} = \frac{1}{\phi + K_{d2}(1-\phi)\rho}$$

K_{d1} : partition coefficient in water column
K_{d2} : partition coefficient in sediment

Appendix G: "Surface Water Quality Monitoring Procedures Manual", TNRCC, June 1999.

Chapter 4. Water Sample collection

Metals-in-Water Samples

When deciding to measure total and dissolved metals, the purpose of the sampling must be considered. Water quality standards for the protection of aquatic life are determined for the dissolved form of heavy metals. The exception to this are mercury and selenium. Water quality standards apply to the total form of mercury and selenium and not the dissolved form. In order to budget inputs, transport, and accumulation of metals, it is necessary to know total metals in the water column, sediments, effluent, etc.

Routine Status Monitoring

For routine status monitoring (sometimes called TSWQS Metals), *dissolved metals* are collected for everything with the exception of mercury and selenium. A total metals sample will need to be collected for these two metals at all routine monitoring sites where metals-in-water are scheduled. Routine metals-in-water samples are not collected during periods of abnormally high turbidity. Samples with high turbidity are unstable in terms of soluble metals and it is difficult to collect a representative grab sample. Special study sampling, however, may be an exception. For example, wet weather sampling is likely to include some samples with high turbidity.

Sample Collection Depth

Collect a metals sample from a depth of one (1) foot using a peristaltic pump. In most streams, near-surface water is representative of the water mass.

For the purpose of determining compliance with numerical toxic substance standards, a sample taken at the surface is adequate.

Sampling Equipment

The filtering procedure must be performed within the holding time, and with extreme care to avoid contamination of the sample. Considering these factors, it is best to use a sampling pump/in-line filter set up. Samples are pumped directly into the sample container. This minimizes contamination by using no intermediate sampling device. Unpowdered latex gloves are always worn during sampling.

Sample Container

The sample container is a one (1) liter plastic bottle. For mercury (only) use 250 ml glass or teflon bottles. Precleaned, preacidified sample containers are commercially available from scientific suppliers. These containers and preservative are rigorously supported up by QC protocols and are best for routine monitoring. Sample containers and lids are soaked in a solution of 5-10% metals grade nitric acid in deionized water and rinsed with metals-free deionized water by the commercial supplier or the laboratory performing the analysis. The containers and tubes are stored and transported in dust-free containers such as a plastic bags.

Equipment Preparation

It is best if the metals-in-water sampling materials are prepared by the laboratory performing the analysis. If a laboratory assembles a Metals-in-Water Sample Collection Kit, it should contain the following items packaged together for each sample:

- Tubing with an in-line (disposable, 0.45 microns) filter attached for dissolved metals-in-water sampling. This same tubing is used for total metals-in-water samples.
- Preacidified sample containers, plastic (4) for total and dissolved samples and blanks; Glass or Teflon (2) for total and dissolved mercury if available
- Acid preservative (if not using preacidified containers)
- Metals-free DI water (for blanks)
- Powder-free latex gloves, two (2) pair

If a laboratory is not assembling collection kits, individuals should take care to keep preacidified containers in the original packaging. When removed from the box, sample containers are placed in plastic bags (Ziploc bags). Although filters come individually wrapped, they should also be stored in a way to avoid possible contamination.

In the laboratory, sample tubes are soaked in a mixture nitric and hydrochloric acid or in a 5-10% solution of reagent grade nitric acid. After soaking, they are rinsed with deionized water. Clean tubing is then put into clean containers, such as, large Ziploc bags. Metalsfree filter cartridges with the capacity to filter several liters are commercially available. Equipment blanks are run at the laboratory on batches of metals-in-water sampling equipment prior to their distribution to field staff. One to two liter containers with metalsfree deionized water are taken into the field for each field blank collected. Metals-free deionized water is supplied by the laboratory performing metals analysis. The deionized water containers are kept clean and dust-free on the outside by wrapping in a plastic bag.

Dissolved Metals-in-Water Collection Technique

Collecting metals-in-water samples requires two people. One person, designated as "**Clean Hands**," is the only one in direct contact with the sampling bottles, tubing and filter (or anything that touches the ambient or blank water). The second person, or "**Dirty Hands**," sets up the apparatus and operates the pump. Both Clean Hands and Dirty Hands wear *powder-free latex gloves* during the sample collection process. If two people are not available to collect metals-in-water samples, they may be collected by an individual if care is taken in the handling of the sampling container, tubing and filter. This may be achieved by changing gloves when switching between Clean Hands/Dirty Hands tasks. Other recommendations discussed in the Clean Hands/Dirty Hands method may also be adapted to an individual sample collector (i.e., tubing and container holders). It is also recommended that samples collected by an individual be submitted with a blank sample. Once it is determined that this method does not introduce contamination in the blanks, the collector may submit blanks according to QC sample requirements for field equipment blanks.

Sample Collection

At the site, **Dirty Hands** sets up the pump while **Clean Hands** takes a bottle from the plastic bag and places it in a "container holder". A container holder can be anything nonmetal that supports the bottle, freeing up the collector's hands.

Clean Hands takes the end of the tubing with the filter attached out of the bag and places it in the pump head. The outlet end is approximately 18 inches from the pump; the other end is long enough to easily reach beneath the water surface. **Dirty Hands** closes the pump head, locking the tubing in place. **Clean Hands** takes the other end of the tubing, removes the plastic cover from the end of the tubing and places it in a “tubing holder”. The tubing holder is a PVC pipe, or something similar (nonmetallic), that can be used to hold and extend the tubing beneath the water surface.

Dirty Hands immerses the intake tube directly into the water and operates the pump to flush the tube and filter with the filter held upright. **Clean Hands** removes the cap from the sample bottle, holds the filter over the container opening and allows the container to fill with 1000 ml (1 liter) of filtrate leaving some head space. **Clean Hands** puts the cap back on the bottle and places it back it in the plastic bag. When ever **Clean Hands** touches the boat or equipment which may be contaminated, gloves should changed immediately.

Sample Preservation

If not using a commercially purchased pre-acidified container, metals-in-water samples are preserved with 2 ml of a 1:1 HNO3/H2O preservative solution made from metals-free nitric acid and deionized water. Fresh water samples require 2 ml of acid preservative and estuarine samples require 4 ml. Samples can be preserved upon arrival at the laboratory. Holding time for acid preserved samples is six (6) months except for mercury which is 28 days. After collecting the sample and adding the preservative, the container is placed back in a plastic bag for shipping. This is to prevent possible contamination from other samples in the ice chest.

Sample Container Label

Label each sample container with the tag number and the type of sample. The preservation method should be noted on the RFA Form. Since the sample has been filtered, write, "field filtered" on the container and indicate if it has preserved. In the space for special instructions on the RFA form, indicate that the sample has been "field filtered and acidified."

Field Equipment Blank

Field blanks are collected at the last site of a sampling trip with the same tube and filter used to collect the last dissolved metals-in-water sample of the day (before the ambient sample is collected); and with the tube used for the last total metals-in-water sample of the day. The same collection method outlined for dissolved and total metalsin-water samples is followed for the field blank with the following exceptions:

Clean Hands opens a cubitainer of blank water (metals-free DI water). **Dirty Hands** removes the plastic cover from the end of the tubing and inserts the tubing into the cubitainer. **Dirty Hands** holds the tubing in place.

Clean Hands takes the plastic cover off the other end of the tubing. **Dirty Hands** turns on the pump and flushes a small amount of water through the filter to purge it for dissolved metals. The same process is followed for total metals-in-water samples but without the filter.

Clean Hands removes the cap from the sample blank bottle and uses the pump to fill it with metals-free deionized (DI) water. **Clean Hands** puts the cap back on the bottle and places it in the plastic bag.

Total Metals-in-Water

For total metals-in-water samples, follow the same procedure used for dissolved metals-in-water but exclude the filter. Collect a total metals-in-water field sample blank whenever total metals are collected. Samples are preserved with metals-free nitric acid as described above. Submit 600-1000 ml of sample for analysis. For mercury, submit 250 mls in a glass or Teflon bottle, filled to the top with no head space. Holding time for preserved samples is six (6) months, except for mercury which is 28 days.

Companion Samples for Metals-in-Water

Request a hardness analysis whenever metals-in-water are to be analyzed from an inland site (Estuarine sites do not require hardness analysis)**.** Typically, the hardness can be calculated from the analysis of calcium and magnesium. Sample holding time for unpreserved samples is 2 days under refrigeration. Label "Total Hardness- Unpreserved". Hardness samples can be preserved giving longer holding times, but they must be filtered before the acid preservative is added. Filter, then preserve with 2 ml of concentrated H2SO4 or 5 ml of concentrated HNO3 per liter of sample. Label "Hardness-Filtered and Preserved with Acid". If a *total metals sample* is collected, submit a sample for TSS if not already requested in a companion sample for "conventionals in water". Sample holding time, under refrigeration, is seven (7) days.

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